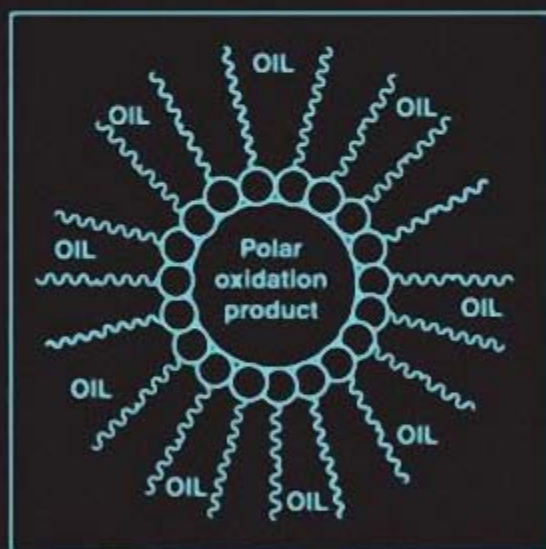


LUBRICANT ADDITIVES

CHEMISTRY AND APPLICATIONS



edited by
Leslie R. Rudnick

LUBRICANT ADDITIVES

CHEMISTRY AND APPLICATIONS

edited by

Leslie R. Rudnick

*The Energy Institute
The Pennsylvania State University
University Park, Pennsylvania, U.S.A.*



MARCEL DEKKER, INC.

NEW YORK • BASEL

Marcel Dekker, Inc., and the author make no warranty with regard to the accompanying software, its accuracy, or its suitability for any purpose other than as described in the preface. This software is licensed solely on an "as is" basis. The only warranty made with respect to the accompanying software is that the CD-ROM medium on which the software is recorded is free of defects. Marcel Dekker, Inc., will replace a CD-ROM found to be defective if such defect is not attributable to misuse by the purchaser or his agent. The defective CD-ROM must be returned within 10 days to: Customer Service, Marcel Dekker, Inc., P.O. Box 5005, Cimarron Road, Monticello, NY 12701, (914) 796-1919.

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress.

ISBN: 0-8247-0857-1

This book is printed on acid-free paper.

Headquarters

Marcel Dekker, Inc.
270 Madison Avenue, New York, NY 10016
tel: 212-696-9000; fax: 212-685-4540

Eastern Hemisphere Distribution

Marcel Dekker AG
Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland
tel: 41-61-260-6300; fax: 41-61-260-6333

World Wide Web

<http://www.dekker.com>

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the headquarters address above.

Copyright © 2003 by Marcel Dekker, Inc. All Rights Reserved.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Preface

I first conceived of writing this book at the close of the last millennium, and it has become a reality in this new millennium, a time in which we have already experienced many changes. Perhaps there is a parallel in the development of additives for lubricants. In the earlier development of additives, the main objectives were to maintain the life of the oil and to protect mechanical components. In the new millennium, these features will be important, but, in addition, the long-term impact of lubricants and additive components will become design and marketing issues based on such concerns as the environment, toxicity, and fuel economy. Development of lubricant and lubricant additives directly from natural and renewable materials will play a far more important role than in the last millennium. Ultimately, it will become desirable to design lubricant materials (base oils and additives) that are derived directly from renewable resources that grow naturally or can be grown in bio-factories. If this type of lubricant could be developed and used on a fill-for-life basis, it could then be recycled with little or no environmental impact. This may seem like a dream, but prior to 1960, so did the use of synthetic lubricants, passenger car transmission oils that would last 200,000 km, and axle or transmission lubes capable of lasting 800,000 km in heavy truck applications. These lubricants are available today.

Additives are materials that impart new and improved properties to lubricants. Continuing demands will be placed on lubricant properties and performance as we move from the end of the 20th century toward the new technologies that await us in this century. One of the current driving forces in the development of new lubricants is protection of the environment. These efforts are driven mostly by government regulations rather than by corporate belief that these are the ultimate

materials of the future. Cost and performance will remain critical aspects of industrial development of petroleum-derived lubricating oils and additives. These demands will result in the synthesis and application of new lubricants and additives necessary to formulate these more stable and better-performing fluids.

It is anticipated that additive development will change from the synthesis of complex mixtures based on petroleum-derived components to the use of naturally occurring or bio-derived components that have antioxidant and corrosion-resistant properties. There are many potent natural antioxidants that could be employed in lubricant fluids to minimize impact on the environment, especially for lower-temperature industrial applications. Cradle-to-grave study (life cycle analysis, LCA) of lubricant, lubricant additives, and lubricant technologies in general will become an integral part of the overall development and evaluation programs of the future. Extreme-pressure additives will present a challenge in terms of being found in nature, but I believe that advances in the synthesis of biodegradable additives will progress, if not from companies in the United States, then from other countries where regulations are more stringent.

The properties and performance of commercialized lubricants are governed by many nonchemical factors, including vehicle manufacturers, regulators, and customers. Collectively, these groups help to provide input on desired lubricant performance. Future developments will require a multidisciplinary effort by equipment builders, regulatory agencies, organic and inorganic chemists, biochemists, and chemical engineers. It will become necessary to rely on input from customers and end users of these new materials to a greater extent than ever before in our history.

Crankcase lubricants and additives will require molecular structures having thermal and oxidative stability sufficient to withstand the rigors of low-heat-rejection, high-performance diesel engines. The lubricants and additives will need to be able to do this with chemistries that have a low environmental impact in terms of both manufacture and disposal of the used oils.

This new century will also experience the application of new types of lubricants, containing new additive chemistries required for space exploration and for development of undersea technologies (perhaps including farming and habitation). These remote locations and extremes of environment will place new demands on lubricant properties and performance and will require low maintenance.

I thank all my colleagues who encouraged me to make this book a reality. I also want to thank all the contributors for responding to the deadlines of this project, knowing the many constraints placed on them by their other responsibilities. There is always a balance between job responsibilities and publishing projects like this one. Again, my heartfelt thank you to everybody involved in this project; it is your contributions that have created this resource for our industry. Essentially all the major classes of currently used lubricant additives are described herein.

I especially want to thank Rita Lazzararo at Marcel Dekker, Inc., with whom I have worked before on '*Synthetic Lubricants and High-Performance Functional Fluids*,' and Erin Nihill, who has provided much needed information and has been a pleasure to work with on this project. Regina Walker also offered excellent advice throughout the project. Thanks also go to Russell Dekker for helpful discussions and for agreeing to support publication of this book.

Thank you, Paula, for remaining my constant companion, and Eric and Rachel for all your interest and support during this project. I enjoy knowing that each of you will continue to create in your own ways and in your own chosen fields of endeavor.

Leslie R. Rudnick

Contents

<i>Preface</i>	<i>iii</i>
<i>Contributors</i>	<i>xi</i>

Part I. Additives: Chemistry, Technology, and Commercial Importance

1. Antioxidants	1
<i>Cyril A. Migdal</i>	
2. Zinc Dithiophosphates	29
<i>Randolph A. McDonald</i>	
3. Ashless Phosphorus-Containing Lubricating Oil Additives	45
<i>W. David Phillips</i>	
4. Detergents	113
<i>Syed Q. A. Rizvi</i>	
5. Dispersants	137
<i>Syed Q. A. Rizvi</i>	

6.	Selection and Application of Solid Lubricants as Friction Modifiers	171
	<i>Gino Mariani</i>	
7.	Organic Friction Modifiers	203
	<i>Dick Kenbeek and Thomas F. Buenemann</i>	
8.	Ashless Antiwear and Extreme-Pressure Additives	223
	<i>Liehpao Oscar Farnag</i>	
9.	Sulfur Carriers	259
	<i>Thomas Rossrucker and Achim Fessenbecker</i>	
10.	Olefin Copolymer Viscosity Modifiers	293
	<i>Michael J. Covitch</i>	
11.	Polymethacrylate Viscosity Modifiers	329
	<i>Bernard G. Kinker</i>	
12.	Tackiness and Antimisting Additives	355
	<i>Frederic A. Litt</i>	
13.	Seal Swell Additives	363
	<i>Jerry K. Sieron and Ronald E. Zielinski</i>	
14.	Biocides as Lubricant Additives	371
	<i>William R. Schwingel</i>	
 Part II. Applications		
15.	Additives for Crankcase Lubricant Applications	387
	<i>Ewa A. Bardasz and Gordon D. Lamb</i>	
16.	Additives for Industrial Lubricant Applications	429
	<i>Joseph M. Perez</i>	
17.	Additives for Food-Grade Lubricant Applications	453
	<i>Michael John Raab and Sibtain Hamid</i>	
18.	Lubricant Additives for Magnetic Recording Disk Drives	467
	<i>Thomas E. Karis and H. S. Nagaraj</i>	
19.	Additives for Grease Applications	513
	<i>Robert Silverstein and Leslie R. Rudnick</i>	

Part III. Trends

20. **Long-Term Trends in Crankcase Additives:
Lubrication for the Future** **541**
*Shirley E. Schwartz, Stella Papasavva,
and Leslie R. Rudnick*
21. **Long-Term Trends in Industrial Lubricant Additives** **557**
Fay Linn Lee and John W. Harris
22. **Long-Term Additive Trends in Aerospace Applications** **587**
*Carl E. Snyder, Jr., Lois J. Gschwender, and
Shashi Kant Sharma*

Part IV. Methods and Resources

23. **Summary of Lubricant Standard Test Methods
and Some Product Specifications** **599**
Leslie R. Rudnick
24. **Lubricant Industry Related Terms and Acronyms** **617**
Leslie R. Rudnick
25. **Internet Resources for the Lubricant Industry** **641**
Leslie R. Rudnick

Index **707**

Contributors

Ewa A. Bardasz The Lubrizol Corporation, Wickliffe, Ohio, U.S.A.

Thomas F. Buenemann Department of Research and Development, Uniqema, Gouda, The Netherlands

Michael J. Covitch, Ph.D. Division of Research, Development, and Testing, The Lubrizol Corporation, Wickliffe, Ohio, U.S.A.

Liehpao Oscar Farng, Ph.D. Corporate Strategic Research, ExxonMobil Research and Engineering Company, Annandale, New Jersey, U.S.A.

Achim Fessenbecker, Ph.D. Business Unit Lubricant Oil Additives, Rhein Chemie Rheinau GmbH, Mannheim, Germany

Lois J. Gschwender, B.S. Nonstructural Materials Branch, United States Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, Ohio, U.S.A.

Sibtain Hamid ANDEROL Company, East Hanover, New Jersey, U.S.A.

John W. Harris, Ph.D. Lubricants Department, Shell Global Solutions US, Houston, Texas, U.S.A.

Thomas E. Karis, Ph.D. Department of Storage Systems and Technology, IBM Research Division, Almaden Research Center, San Jose, California, U.S.A.

Dick Kenbeek, ING. Department of Research and Development, Uniqema, Gouda, The Netherlands

Bernard G. Kinker RohMax USA., Inc., Horsham, Pennsylvania, U.S.A.

Gordon D. Lamb BP Castrol, Pangbourne, England

Fay Linn Lee, Ph.D. Lubricants Department, Shell Global Solutions US, Houston, Texas, U.S.A.

Frederic A. Litt, Ph.D. Functional Products Inc., Macedonia, Ohio, U.S.A.

Gino Mariani Acheson Colloids Company, Port Huron, Michigan, U.S.A.

Randolph A. McDonald Functional Products, Inc., Macedonia, Ohio, U.S.A.

Cyril A. Migdal, Ph.D. Department of Petroleum Additives, Crompton Corporation, Middlebury, Connecticut, U.S.A.

H. S. Nagaraj, Ph.D. IBM Storage Systems Division, San Jose, California, U.S.A.

Stella Papasavva, Ph.D. Research and Development and Planning Center, General Motors, Warren, Michigan, U.S.A.

Joseph M. Perez, Ph.D. Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.

W. David Phillips, B.Sc., F.Inst. Pet. Department of Performance Additives and Fluids, Performance Additives and Fluids Business, Great Lakes Chemical Corp., Manchester, England

Michael John Raab, B.S., M.B.A. ANDEROL Company, East Hanover, New Jersey, U.S.A.

Syed Q. A. Rizvi, Ph.D. King Industries, Inc., Norwalk, Connecticut, U.S.A.

Thomas Rossrucker Business Unit Lubricant Oil Industry, Rhein Chemie Rheinau GmbH, Mannheim, Germany

Leslie R. Rudnick, Ph.D. The Energy Institute, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.

Shirley E. Schwartz, Ph.D. General Motors Powertrain, Warren, Michigan, U.S.A.

William R. Schwingel The Dow Chemical Company, Buffalo Grove, Illinois, U.S.A.

Shashi Kant Sharma, Ph.D. United States Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, Ohio, U.S.A.

Jerry K. Sieron, B.S. Department of Engineering, Universal Technology Corporation, Dayton, Ohio, U.S.A.

Robert Silverstein The Orelube Corporation, Plainview, New York, U.S.A.

Carl E. Snyder, Jr., M.Sc. Nonmetallic Materials Division, United States Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, Ohio, U.S.A.

Ronald E. Zielinski, Ph.D. PolyMod® Technologies Inc., Fort Wayne, Indiana, U.S.A.

PART I

ADDITIVES: CHEMISTRY, TECHNOLOGY, AND COMMERCIAL IMPORTANCE

Antioxidants

CYRIL A. MIGDAL

Crompton Corporation, Middlebury, Connecticut, U.S.A.

1 INTRODUCTION

Well before the mechanism of hydrocarbon oxidation was thoroughly investigated, researchers had come to understand that different oils provided greater resistance to oxidation than others. The difference was eventually identified as naturally occurring antioxidants, which varied depending upon crude source or refining techniques. Some of these natural antioxidants were found to contain sulfur-or nitrogen-bearing functional groups. Therefore, it is not surprising that certain additives used to impart special properties to the oil, such as sulfur-bearing chemicals, were found to provide additional antioxidant stability. The discovery of sulfurized additives providing oxidation stability was followed by similar properties identified in phenol. This led to the development of sulfurized phenols. Next certain amines and metal salts of phosphorus-or sulfur-containing acids were identified as imparting oxidation stability. By now numerous antioxidants for lubricating oils have been patented and described in the literature. One of the most important aspects of lubricating oils is that the oxidation stability be maximized. Exposure of hydrocarbons to oxygen and heat will accelerate the oxidation process. The internal combustion engine is an excellent chemical reactor for catalyzing the process of oxidation. Also, the engine's metal parts, such as copper and iron, act as effective oxidation catalysts. Thus, engine oils are probably more susceptible to oxidation than any other lubricant application. However, any lubricating oil exposed to air and heat will eventually oxidize. Antioxidants are the key additive that protects the lubricant from oxidative degradation, allowing the fluid to meet the demanding requirements for use in engines and industrial applications. Several effective antioxidants classes have been developed over the years and have seen use in engine oils, automatic transmission fluids, gear oils,

turbine oils, compressor oils, greases, hydraulic fluids, and metal-working fluids. The main classes of oil-soluble organic and organometallic antioxidants are the following types:

1. Sulfur compounds
2. Phosphorus compounds
3. Sulfur-phosphorus compounds
4. Aromatic amine compounds
5. Hindered phenolic compounds
6. Organo-alkaline earth salt compounds
7. Organozinc compounds
8. Organocopper compounds
9. Organomolybdenum compounds

2 SULFUR COMPOUNDS

The initial concepts of using antioxidants to inhibit oil oxidation date back to the 1800s. One of the earliest inventions described in the literature [1] is heating a mineral oil with elemental sulfur to produce a nonoxidizing oil. However, the major drawback to this approach is the high corrosivity of the sulfurized oil toward copper. A combination antioxidant and corrosion inhibitor was developed by sulfurizing sperm oil [2]. Similarly, terpenes and polybutene have also been treated with sulfur [3a-c]. Paraffin was also employed to prepare sulfur compounds [4a-d]. Typical structures of several sulfur compounds are illustrated in Figure 1. These can be complex chemical mixtures, but for purposes of simplification, the theoretical structures are shown.

Aromatic and aliphatic sulfides represent another class of additive used as oxidation and corrosion inhibitors. Some example are simple sulfur-containing aromatics such as dibenzyl sulfide, dixylyl disulfide, or dicetyl sulfide. More complex compounds of a similar type are the alkyl phenol sulfides [5a-e]. Alkyl phenols, such as mono- or di-butyl, -amyl, or -octyl phenol have been reacted with sulfur mono- or dichloride forming either mono- or disulfides. As shown in Figure 1, the aromatic sulfides such as benzyl sulfide have the sulfur attached to carbon atoms in the alkyl side groups, whereas the alkyl phenol sulfides have the sulfur attached to carbon atoms in the aromatic rings. In general, the alkyl phenol sulfide-type structure appears to have superior antioxidant properties in many types of lubricants. The hydroxyl groups in the alkyl phenol sulfides may also be treated with metals to form oil-soluble metal phenates. These metal phenates play the dual role of detergent and antioxidant.

A multifunctional antioxidant extreme-pressure additive was prepared by sulfurizing norbornene, 5-vinylnorbornene dicyclopentadiene, or methyl cyclopentadiene dimer [6]. Heterocyclic compounds such as *n*-alkyl 2-thiazoline disulfide in combination with the zinc salts of dialkyldithiophosphoric acid (ZDDP) have provided excellent antioxidant laboratory engine testing [7]. Sulfur- and oxygen-containing compositions derived from beta-thiodialkanol have been found to be superb antioxidants in automatic transmission fluids [8]. Novel dihydrobenzothio-phenes prepared via condensation of low-cost arylthiols and carbonyl compounds

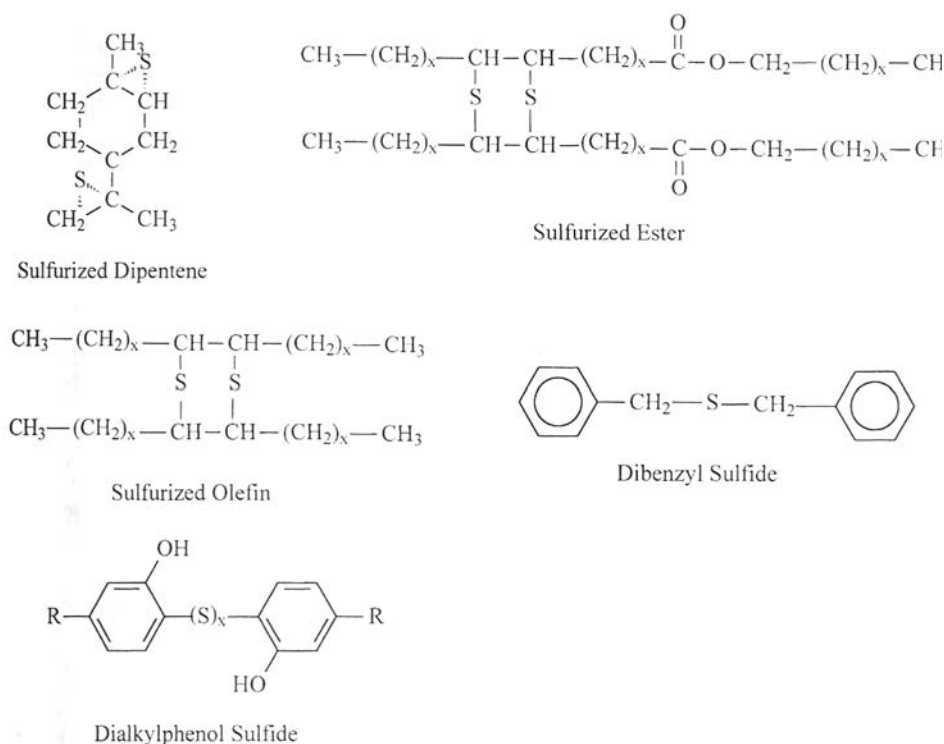


Figure 1. Sulfur-bearing antioxidants.

in a one-step, high-yield process have proven to be effective antioxidant and antiwear additives [9].

3 PHOSPHORUS COMPOUNDS

The good performance of phosphorus as an oxidation inhibitor in oils was identified early in lubrication science. The use of elemental phosphorus to reduce sludge formation in oils has been described [10]. However, elemental phosphorus, like elemental sulfur, may have corrosive side effects to many nonferrous metals and alloys, so it is rarely incorporated in oils in this form; rather oil-soluble organic compounds of phosphorus are preferred. Alkyl and aryl phosphites, such as tributyl phosphite and triphenyl phosphite, are efficient antioxidants in some petroleum base oils, and many patents have been issued on such compositions [11a,b]. Naturally occurring phosphorus compounds such as lecithin have also been utilized as antioxidants, and many patents have been issued on these materials either alone or in combination with other additives [12a-d]. Lecithin is a phosphatide produced commercially as a byproduct from the processing of crude soybean oil. The aluminum, calcium, or barium salts of alkyl phosphoric acids are another type of phosphorus compound that displays antioxidant properties [13a,b].

4 SULFUR-PHOSPHORUS COMPOUNDS

After a wide variety of both sulfur and phosphorus compounds was identified that provided antioxidant protection to hydrocarbons, the next step in the development of antioxidants was the utilization of oil-soluble organic compounds containing both sulfur and phosphorus. Numerous patents have been issued on such compositions, and a considerable number have been used commercially [14a–h]. In fact, the antioxidants containing both sulfur and phosphorus are usually more effective and efficient in a wider variety of base stocks than those containing only phosphorus or sulfur, and many commercial oils have used one kind or other of these sulfur-phosphorus-type additives.

One widely used class of sulfur-phosphorus additive is the dialkyldithiophosphates, which are prepared by the reaction of phosphorous pentasulfide with high-molecular-weight alcohols. This is shown in Figure 2. Since this reaction yields dithiophosphoric acids, metal salts such as zinc, barium, or calcium are the preferred additives. Many type of alcohols, such as the aliphatic, cyclic [14c], and phenol derivatives have been used, and those of fairly high molecular weight (such as lauryl, octyl, cyclohexyl, methyl cyclohexyl alcohols, and amyl [14f] or butyl phenols) are preferred in order to yield dithiophosphates with good solubility characteristics in oils.

Numerous patents describe the reaction of phosphorus pentasulfide with unsaturated organic compounds, such as the terpenes, polybutenes, wax olefins, fatty acids, fatty esters, sperm oil, etc [15a–v]. During these reactions, hydrogen sulfide is liberated and the reaction products are usually acidic. The mechanism of the P_2S_5 reaction with olefins in these cases may be one of substitution (replacement of reactive hydrogen atoms) as well as of addition. In preparing the additives, these acidic reaction mixtures were neutralized by treatment with alkaline earth hydroxides so that metal salts are formed. Calcium, barium, or potassium salts have been preferred. Some additives of this type also display detergency characteristics. The large amount of patent activity in this area demonstrates the wide variety of products derived from the reaction of phosphorus pentasulfide and an unsaturated organic moiety to yield an antioxidant composition in oil. Several of these, particularly the terpene and polybutene reaction products, have been used extensively commercially. The addition products with terpenes may be quite varied in exact chemical structure.

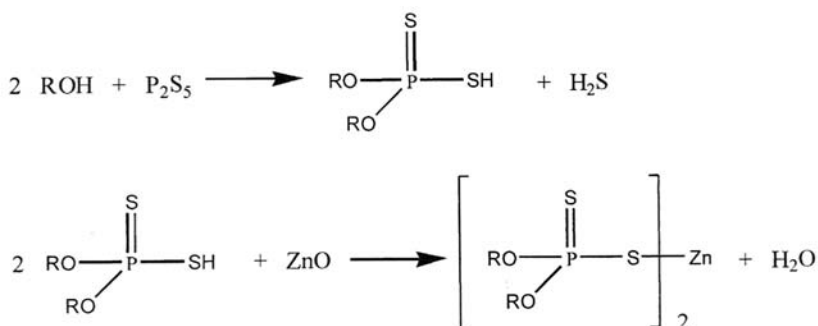


Figure 2. Zinc dialkyldithiophosphate synthesis.

A key component of the oxidation inhibitor package for engine oils and transmission fluids today is the metal salts of thiophosphoric acids. For over 60 years they have been one of the most cost-effective antioxidants. In addition, the zinc salts of dialkyldithiophosphoric acids (ZDDP) show good antiwear properties, especially in the valve train area. The salts of C4/C5 dialkyldithiophosphoric acid have been the most common, but a broad range of other alkyl and aryl derivatives has been developed to meet special needs such as protection at high temperatures. The same sulfide or phosphate films formed by these materials, and which are responsible for their antiwear properties, also provide protection against corrosion by organic acids formed during the oxidation process.

It has been shown that the corrosive attack and metal staining of ZDDP can be reduced by addition of alkyl or aryl phosphates during the synthesis [16]. For example, phenyl phosphate is added to the dialkylphosphoric acid and heated at 110°C for an hour before the zinc oxide is added. Another patent describes a novel dithiophosphate of improved oxidation stability [17]. An acid is reacted with a glycol, to give a monoester having a hydroxyl group, which is then reacted with P_2S_5 to give the dialkyldithiophosphoric acid. This acid is then reacted with zinc oxide, to give the novel dithiophosphates. To improve solubility, salts can be made of lower dialkyldithiophosphates by using both primary and secondary alcohols in the process [18]. The purpose is to increase the ratio of zinc to phosphorus in the salt. In addition, a small amount of butyl alcohol is added to ensure solubility of the product. Furthermore, mixed metal salts of dialkyldithiophosphoric acids and carboxylic acids are claimed to have higher thermal stability [19].

Many descriptions have recently appeared of organomolybdenum complexes that impart excellent oxidation stability to lubricants. The combination of ZDDP with a molybdenum containing adduct, prepared by reacting a phosphosulfurized polyisoalkylene or alpha olefin with a molybdenum salt, is described [20]. The molybdenum adduct alone gave poor performance in oxidation tests, but the mixture with ZDDP provided good oxidation stability. Certain molybdenum additives show good oxidation resistance and acceptable corrosion, when prepared by reacting water, an acidic molybdenum compound, a basic nitrogen complex, and a sulfur source [21a,b]. When the additive is combined with an aromatic amine, it provides enhanced antioxidant properties in oxidation tests [22]. Molybdenum dialkyldithiocarbamates (C_{7-24}) and alkylated diphenylamines are claimed broadly in lubricating oils [23]. More restrictive are claims for molybdenum dialkyldithiocarbamates (C_{8-23} and/or C_{3-18}) and alkylated diphenylamines in lubricating oils that contain less than 3 wt% aromatic content and less than 50 ppm sulfur and nitrogen [24]. Molybdenum dialkyldithiocarbamates and hindered phenolic antioxidants are claimed together in lubricating oils that contain 45 wt% or more, one or two ring naphthenes, and less than 50 ppm sulfur and nitrogen [25]. The combination of alkylated diphenylamines, sulfurized olefin or hindered phenolic, and oil-soluble molybdenum compounds is claimed to be a highly effective antioxidant combination, especially for highly saturated, low-sulfur base oils [26]. Sulfur-free molybdenum compounds, such as molybdenum carboxylates, have also been identified as antioxidant synergists with alkylated diphenylamines in lubricating oils [27a,b]. Novel organomolybdenum complexes prepared with vegetable oil have been identified as synergistic with alkylated diphenylamines and ZDDPs in lubricating oils [28].

5 AMINES AND PHENOL DERIVATIVES

Oil-soluble organic amines and phenol derivatives, such as pyrogallol, gallic acid, dibutylresorcinol, hydroquinone, diphenylamine, phenyl- α -naphthylamine, and beta-naphthol, are early examples of antioxidants used in turbine oils and lubricating greases [29a,b]. In engine oils these types of compounds showed only limited effectiveness. Other amines and phenol derivatives such as tetramethyldiaminodiphenylmethane and alizarin were used to some degree as antioxidants for engine oils. However, these compounds were rarely used alone but were used in combination with other types of antioxidants. For example, a mixture of a complex amine with a phosphorus pentasulfidepolybutene reaction product has been reported [30]. Another reported mixture is a complex phenol derivative such as alizarin in combination with an alkyl phenol sulfide and a detergent additive [31].

Aromatic diamines, such as 3,5-diethyltoluenediamines, where the amino groups are unsubstituted except for hydrogen, have been claimed to be beneficial. Laboratory oxidation tests show low viscosity increases and low bearing-weight losses using up to 1% of the inhibitor [32]. Substituted benzylamines or substituted 1-amino-1, 2, 3, 4-tetrahydronaphthalene are particularly useful in synthetic lubricants such as polyalphaolefins or polyol esters. They are preferably used in combination with a metal salt and a metal deactivator. Test data demonstrate very low metal corrosion, low viscosity increase, and low sludge buildup [33]. *N,N'*-diphenyl-*p*-phenylenediamines where the phenyl groups may be substituted with methyl, ethyl, or methoxy have been claimed as effective antioxidants [34]. 2,3-dihydroperimidines prepared from the condensation of 1,8-diaminonaphthalenes with ketones or aldehydes show good oxidation inhibition in the Rotary Bomb Oxidation Test (RBOT; ASTM D-2272). Synergistic behavior was also shown observed with phenolic and amine inhibitors [35]. *N,N'*-disubstituted-2,4-diaminodiphenyl ethers and imines of the same ethers have shown low viscosity increase, low acid number, and reduced metal corrosion in bench tests [36a,b]. The reaction product of a hydrocarbyl succinic anhydride and 5-amino-triazole demonstrated effectiveness as an antioxidant in a railway diesel oil composition [37].

Alkylated diphenylamines have been workhorse antioxidants for engine oils for two decades. The typical synthesis of alkylated diphenylamines begins with benzene, which is first converted to aniline, followed by a very high-temperature conversion to diphenylamine. Next the diphenylamine under acidic conditions (with heat) can be treated with a variety of olefins. The most common are isobutylene, diisobutylene, nonenes, styrene, or propylene tetramer. Depending on the acidic catalyst, olefin, and other reaction conditions, the degree and position of alkylation will vary from mono- to di-alkylation.

Oligomeric versions prepared from diphenylamines have been described for use in ester lubricants; they are claimed to be more desirable than simple diphenylamines for extremely high-temperature applications [38]. Advances in the preparation of alkylated diphenylamines continue, with the use of novel clay catalyst to produce high levels of mono-alkylated diphenylamines with lower levels of di-alkyl diphenylamines and undesirable unsubstituted diphenylamine [39].

Several patents based on benzotriazoles have been issued. Examples are *N-t*-alkylated benzotriazoles and the adduct of benzotriazole with an alkyl vinyl ether or a vinyl ester of a carboxylic acid such as vinyl acetate [40a,b]. Triazole adducts

of an amine phosphate or of an adduct of salts of organodithiophosphate have also been claimed [41a–b]. Data generated in the RBOT oxidation test (ASTM D-2272) and TOST sludge test (ASTM D-943-2) for the reaction products of an alkylated aryl amine and an aldehyde show that alkylated naphthyl amines are superior to diphenyl amines [42].

Many complex phenolic compounds have been in claims, such as oxidatively coupled products of hydroxy aromatic compounds [43]. The combinations of phenols and sulfur chemistry have also been widely reported. For example, the reaction products of hindered phenols with selected thioalkenes have shown in oxidation tests low increases in acid neutralization number, low viscosity increases, and effectively no lead corrosion [44]. Another patent combining sulfur and phenolic activity describes a process for preparing hydrocarbylthio-substituted phenols by reacting substituted phenols with hydrocarbyl disulfides using as aluminum phenoxide catalyst [45]. Oxidation test results showed lower viscosity increases and bearing-weight losses compared with 4,4'-methylene bis (2,6-di-tertiarybutylphenol). The importance of chlorine-free additives has led to the development of oil-soluble, chlorine-free, sulfurized hindered phenolic antioxidants that do not impart excessive corrosion [46].

The combination of both amine and hindered phenolic moieties in one molecule has been disclosed, which provides improved thermal stability, oil solubility, and lower volatility [47]. Phenolic imidazolines have been prepared from phenolic amines and carbonyl compounds. In addition to providing antioxidant activity, they also act as corrosion inhibitors and metal deactivators due to the presence of the cyclic imidazoline group [48]. Also, combinations of sulfur and nitrogen in one molecule have been considered effective antioxidants. Phenothiazines are well-known antioxidants of this type that have found use in aviation fluids. Recent advances have led to *N*-substituted thio alkyl phenothiazines with improved oil solubility [49] as well as *N*-aminopropylphenothiazine, useful for further derivatization of the *N*-amino group [50]. For example, novel derivated phenothiazines can be attached to olefin copolymers to act as a multifunctional VI improver for lubricants [51]. Another example of a multifunctional additive combines sulfur, nitrogen, and phenolic moieties all in one molecule. In this instance mercaptobenzothiazoles or thiadiazoles are Mannich reacted with hindered phenolic antioxidants to yield oil-soluble antioxidant and antiwear additives [52].

6 COPPER ANTIOXIDANTS

One variation of the sulfur inhibitors described above was the development of a group of copper-sulfur complexes formed by sulfurizing certain types of unsaturated organic compounds in the presence of copper [53a–c]. Complex oil-soluble compounds containing both sulfur and copper were formed; they act as efficient inhibitors in certain types of base stocks. This type of inhibitor additive is particularly interesting since copper normally acts as a pro-oxidation catalyst [70].

Several patents also describe the use of copper, which is usually considered a pro-oxidant and is a catalyst in some laboratory oxidation tests. A lubricating composition has been disclosed which contains from 0.01 and 5.0 parts by weight of a zinc hydrocarbyl dithiophosphate (ZDDP) and from 60 to 200 parts per million of copper [54]. Data are given for an oxidation test using a fully formulated

oil containing ZDDP and a variety of supplemental antioxidants including amines, phenolics, a second ZDDP, and various copper salts. Only the blends with the copper salts passed the oxidation test. With the other additives the viscosity increase was excessive. In addition, engine test results showed that below 60 ppm copper the increase in viscosity was excessive, while greater than 200 ppm copper gave excessive cam and lifter wear. In another patent, copper was complexed with a mono-oxazoline, bis-oxazoline, or lactone oxazoline dispersant [55], resulting in improved oxidation stability. The copper salt of a substituted succinic anhydride derivative containing at least one free carboxylic acid group, when put into a engine oil, passed rust, oxidation, and corrosion engine testing [56].

7 THE MECHANISM OF ANTIOXIDANT ACTION

Lubricating oils are susceptible to degradation by oxygen [57]. The oil oxidation process is the major cause of oil thickening. This manifests itself as sludge and varnish formation on engine parts, leading to increased engine wear, poor lubrication, and reduced fuel economy. Antioxidants are essential additives incorporated into lubricant formulations to minimize and delay the onset of lubricant oxidative degradation. Next we discuss the mechanism of lubricant degradation and that of its stabilization by antioxidants.

8 AUTO-OXIDATION OF LUBRICATING OIL

The well-documented auto-oxidation mechanism involves a free-radical chain reaction [57,58,72]. It consists of four distinct reaction steps: chain initiation, propagation, branching, and termination.

8.1 Initiation



The initiation step occurs due to transfer of energy in the form of heat, UV light, or mechanical shear stress to a hydrocarbon molecule [62]. This process can be catalyzed by the presence of metal ions. The ease of homolytic cleavage of an R-H bond to form two radicals is determined by C-H bond strength and resulting radical stability. Tertiary hydrogens, or those in an alpha position to a carbon-carbon double bond or aromatic ring, are most susceptible.

8.2 Chain Propagation

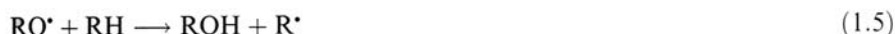


The first propagation step involves an alkyl radical reacting irreversibly with oxygen to form an alkyl peroxy radical. The reaction of the alkyl radical with oxygen is extremely fast; the specific rate depends on the radical's substituents [57]. The second propagation step is the hydrogen abstraction from a hydrocarbon molecule by an

alkyl peroxy radical to form a hydroperoxide and another alkyl radical. Generally, the alkyl peroxy radicals are in greater concentration than the alkyl radicals. This is due to the combination of high oxygen concentration and the faster reaction rate of oxygen with alkyl radical than the slow reaction rate of alkyl peroxy radical with hydrocarbon.

8.3 Chain Branching

8.3.1 Radical Formation



8.3.2 Aldehyde or Ketone Formation



The chain-branching steps begin with the cleavage of hydroperoxide into alkoxy and hydroxy radicals. This reaction has a large activation energy and only is significant at temperatures greater than 150°C. The alkoxy and hydroxy radicals then can react with hydrocarbons to form more alkyl radicals, alcohols, and water. Secondary and tertiary alkoxy radicals will readily form aldehydes and ketones, respectively. These aldehydes and ketones condense via acid catalyzed aldol reactions. These condensates can lead to polymeric degradation products that eventually manifest themselves as sludge and varnish deposits in engines.

8.4 Chain Termination



Chain termination can occur via the combination of radicals. Two alkyl radicals can combine to form a hydrocarbon molecule. Alternatively, an alkyl radical can combine with an alkyl peroxy radical to form a peroxide, or two alkyl peroxy radicals can combine to form a peroxide with evolution of oxygen. However, peroxides easily break down and generate more alkyl peroxy radicals.

9 METAL CATALYSIS OF LUBRICANT DEGRADATION

Metal ions are able to catalyze the initiation step as well as the hydroperoxide decomposition in the chain-branching step [59]. They are able to achieve this via a redox mechanism illustrated below. The required activation energy is lowered for this mechanism, and the initiation and propagation steps thus commence at much lower temperatures.

9.1 Metal Catalysis

9.1.1 Initiation Step



9.1.2 Propagation Step



10 HIGH-TEMPERATURE LUBRICANT DEGRADATION

The preceding discussion provides the basis for the auto-oxidation stage of lubricant degradation under both low- and high-temperature conditions. The end result of low-temperature oxidation is the formation of peroxides, alcohols, aldehydes, ketones, and water [60,66]. Under high-temperature oxidation conditions, acids form during the latter stages of lubricant degradation. Next, the oil's volatility and viscosity increase, and sludge and varnish develop. One way that acids are formed is via the reaction of an alkyl peroxy radical with an aldehyde [57], as shown in Figure 3. Figure 4 illustrates the formation of sludge precursors via acid- or base-catalyzed aldol condensation from aldehydes and/or ketones [57]. Initially $\alpha\beta$ -unsaturated aldehydes or ketones form, and further reaction of these species lead to high-molecular-weight products. These products contribute to an oil viscosity increase. Eventually they combine with each other, leading to sludge and varnish formation.

11 OXIDATION INHIBITION

The proceeding lubricant degradation mechanism makes clear several possible counter measures to control lubricant degradation. Blocking the energy source is one path but is effective only for lubricants used in low-shear and temperature situations. However, more practical for most lubricant applications are the trapping of catalytic impurities and the destruction of hydrocarbon radicals, alkyl peroxy radicals, and hydroperoxides. This can be achieved through the use of radical scavengers, peroxide decomposers, and metal deactivators.

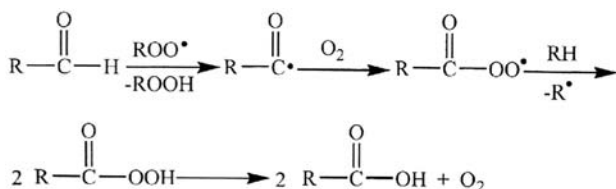


Figure 3. High-temperature lubricant degradation ($>120^{\circ}\text{C}$).

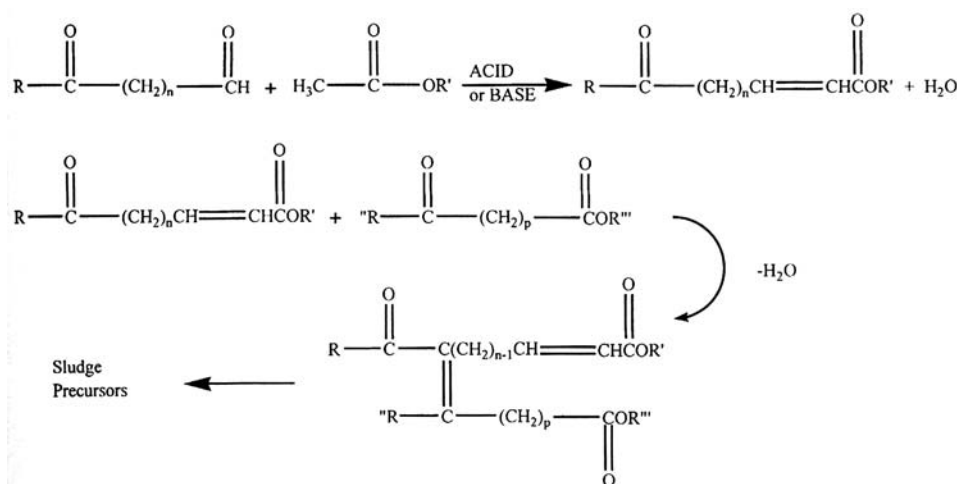


Figure 4. High-temperature lubricant degradation (>120°C).

The radical scavengers are known as *primary antioxidants*. They donate hydrogen atoms that react with alkyl radicals and/or alkyl peroxy radicals, interrupting the radical chain mechanism of the auto-oxidation process. The primary antioxidant then becomes a stable radical, the alkyl radical becomes a hydrocarbon, and the alkyl peroxy radical becomes an alkyl hydroperoxide. Hindered phenolics and aromatic amines are the two chemical classes of primary antioxidants for lubricants. The transfer of a hydrogen from the oxygen or nitrogen atom to the radical forms quinones or quinoneimines that do not maintain the radical chain mechanism.

The peroxide decomposers are known as *secondary antioxidants* [58]. Sulfur and/or phosphorus compounds reduce the alkyl hydroperoxides in the radical chain to alcohols while being oxidized in a sacrificial manner. Zinc dialkyldithiophosphate, phosphites, and thioethers are examples of different chemical classes of secondary antioxidants.

There are two types of metal deactivators: chelating agents [58] and film-forming agents [67]. The chelating agents will form a stable complex with metal ions, reducing the catalytic activity of the metal ions. Thus, the deactivators can show an antioxidant effect. Film-forming agents act two ways. First, they coat the metal surface, thus preventing metal ions from entering the oil. Second, they minimize corrosive attack of the metal surface by physically restricting access of the corrosive species to the metal surface. Disalicylidene propylene diamine is an example of a chelating agent. Substituted benzotriazole is an example of a film-forming agent.

12 MECHANISMS OF PRIMARY ANTIOXIDANTS

12.1 Hindered Phenolics

A classical example of a hindered phenolic is 3,5-di-*t*-butyl-4-hydroxytoluene (2,6-di-*t*-butyl-4-methylphenol), also known as BHT. [Figure 5](#) compares the reaction of an alkyl radical with BHT versus oxygen. The reaction-rate constant of alkyl radical

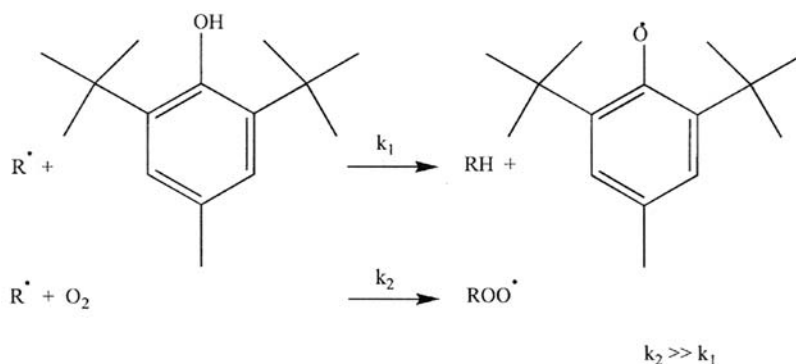


Figure 5. Phenolic reactivity.

with oxygen to form alkyl peroxy radicals is much greater than the reaction-rate constant of alkyl radical with BHT [57]. Hence, in the presence of oxygen there is very little reaction of BHT with hydrocarbon radicals. Instead, BHT and other hindered phenolics donate a hydrogen atom to the alkyl peroxy radical and trap it, as shown in Figure 6. Note that the phenoxyl radical of BHT is stabilized through steric hindrance and resonance structures. The cyclohexadienone radical resonance structure can combine with a second alkyl peroxy radical to form the cyclohexadienone alkyl peroxide, which is stable at temperatures less than 120°C [61]. Figure 7 illustrates the high-temperature decomposition of cyclohexadienone alkyl peroxide to alkoxy radical, alkyl radical, and 2,6-di-*t*-butyl-1,4-benzoquinone. Two phenoxyl radical

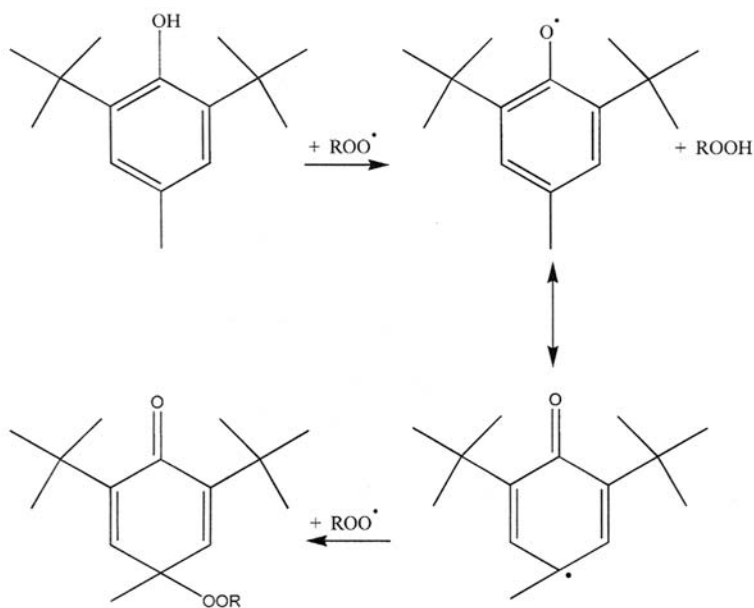


Figure 6. Hydrogen donor and peroxy radical trap.

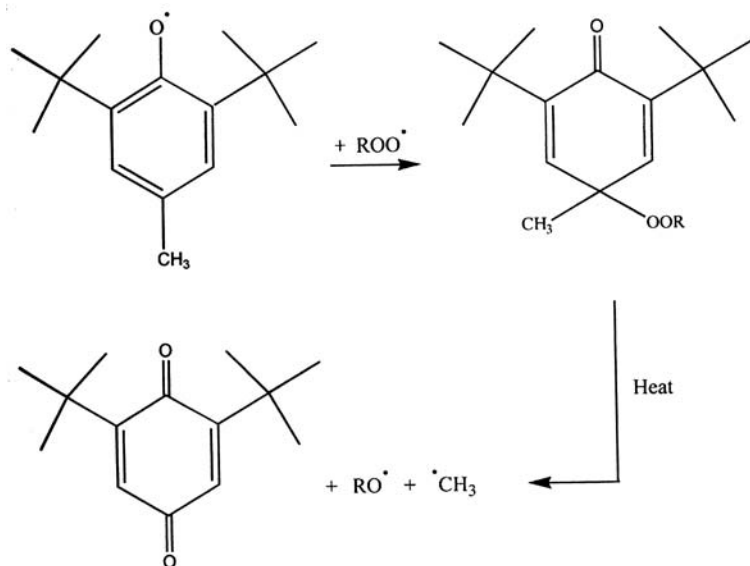


Figure 7. Peroxide decomposition.

resonance structures can undergo the chain termination step shown in [Figure 8](#). One of the phenoxy radicals can donate a hydrogen atom to the other, thus regenerating one BHT molecule and one methylene cyclohexadienone.

13 AROMATIC AMINES

A particularly effective class of aromatic amines useful as primary antioxidants is the secondary aromatic amines commonly referred to as alkylated diphenylamines [62]. The reaction mechanism of oxidation inhibition by alkylated diphenylamines begins with hydrogen atom abstraction by alkyl radical, alkyl peroxy radical, and alkoxy radical as illustrated in [Figure 9](#). Due to the high concentration of alkyl peroxy radical, it reacts with alkylated diphenylamine to form the aminyl radical and alkyl hydroperoxide predominates. [Figure 10](#) shows the next five steps of the low-temperature ($<120^\circ\text{C}$) oxidation inhibition mechanism [57, 65]. In the second step, aminyl radical reacts with a second alkyl peroxy radical, forming a nitroxyl radical and an alkoxy radical. The nitroxyl radical is stabilized through three resonance structures [62, 65], illustrated in [Figure 11](#). In the third step, a third alkyl peroxy radical reacts with the nitroxyl radical, forming a nitroxyl-peroxide complex. In the fourth step, the nitroxyl-peroxide complex eliminates an ether molecule, forming a nitroxyl cyclohexadienone. In the fifth step, a fourth alkyl peroxy radical adds to the nitroxyl cyclohexadienone. In the last step, the nitroxyl cyclohexadienone peroxide dissociates to form 1,4-benzoquinone and an alkylated nitrosobenzene. Therefore, on an equimolar basis, in theory, alkylated diphenylamines can quench twice as many alkyl peroxy radicals as a mono hindered phenolic under low-temperature conditions.

[Figure 12](#) illustrates that at high temperatures ($>120^\circ\text{C}$) the nitroxyl radical is able to react with a secondary alkyl radical to form an *N*-sec-alkoxy diphenylamine

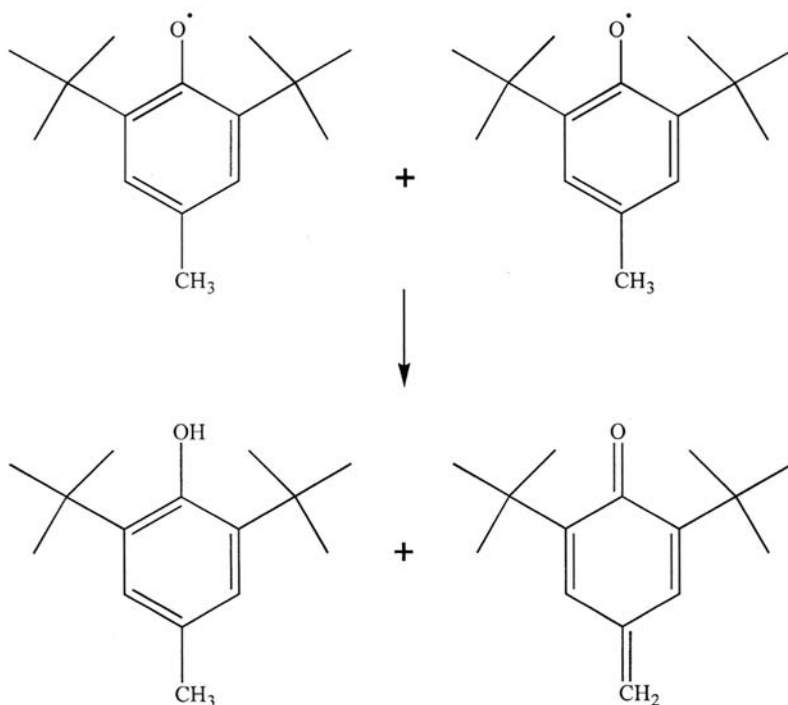


Figure 8. Chain termination.

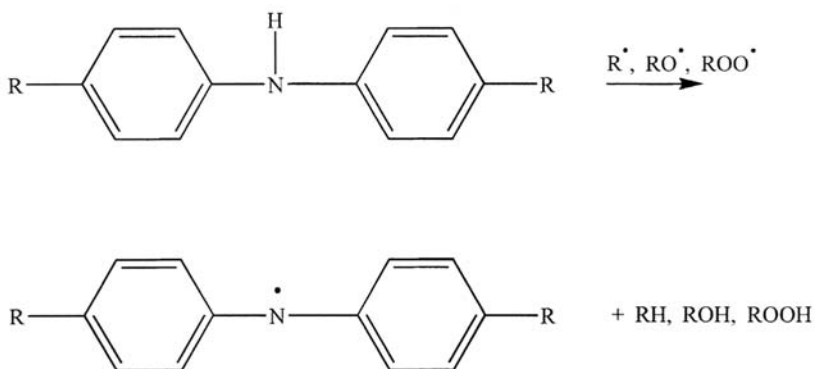


Figure 9. Diphenylamine as a hydrogen donor.

intermediate [57, 63, 66]. This intermediate then thermally rearranges to form a ketone and regenerate alkylated diphenylamine. Thus, at high temperatures, one complete inhibition cycle traps one alkyl peroxy and one alkyl radical. The alternative pathway for reaction of the nitroxyl radical discussed for the low-temperature mechanism competes with this regeneration process. However, this regeneration process can provide alkylated diphenylamines with a stoichiometric efficiency of over 12 radicals per molecule of alkylated diphenylamine [66].

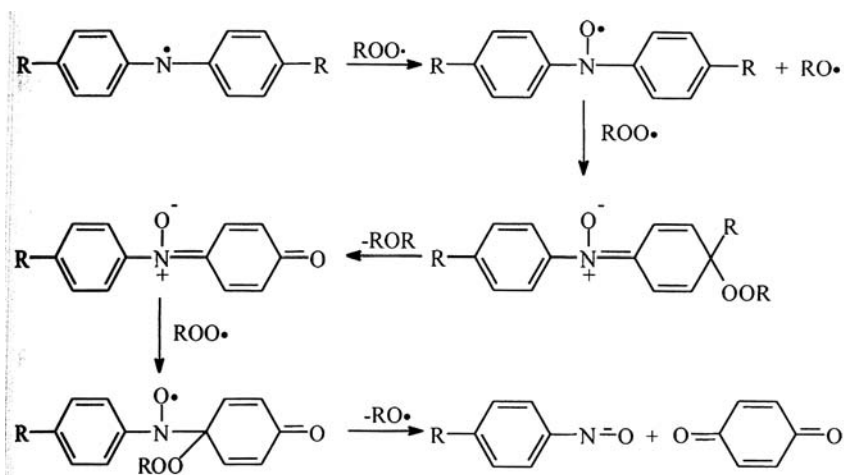


Figure 10. Low-temperature mechanism.

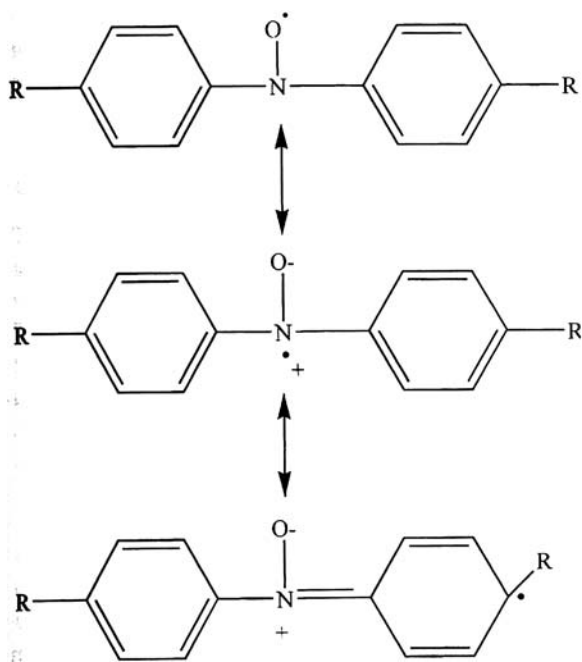


Figure 11. Nitroxyl resonance structures.

Figure 13 illustrates that at high temperatures (>120°C) the nitroxyl radical is able to abstract a hydrogen atom from a tertiary alkyl radical to form an *N*-hydroxyl diphenylamine and an alkene. The *N*-hydroxyl diphenylamine then can react with an alkyl peroxy radical to regenerate the nitroxyl radical and an alkyl hydroperoxide.

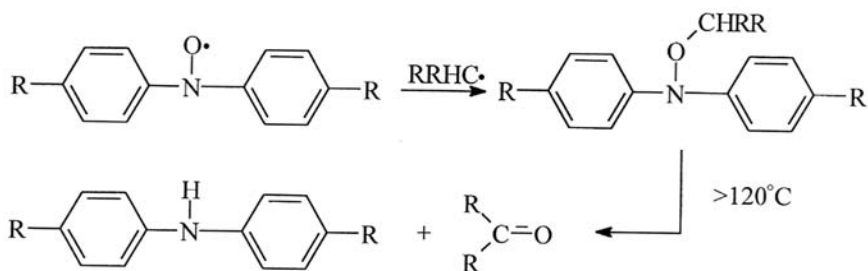


Figure 12. High-temperature mechanism.

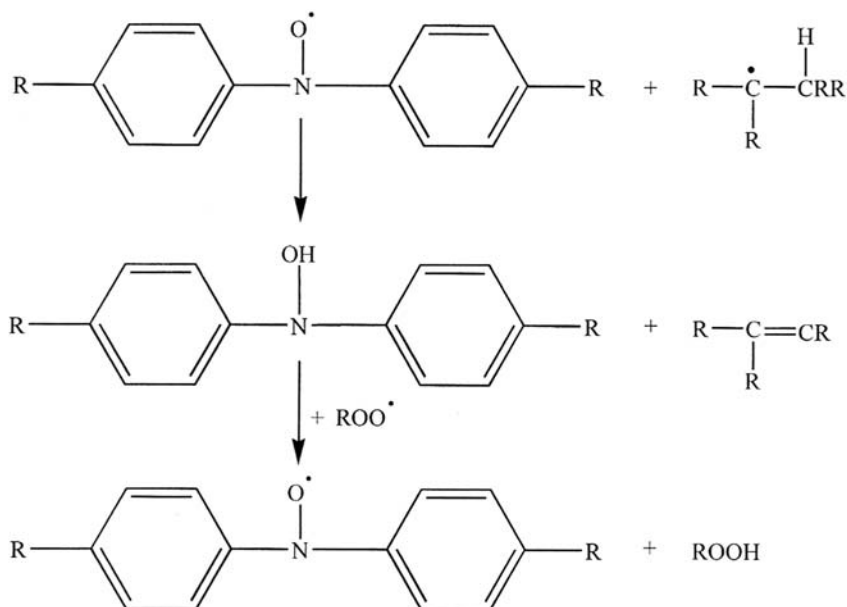


Figure 13. Hydroxylamine formation.

14 SYNERGISM BETWEEN AROMATIC AMINE AND HINDERED PHENOLIC ANTIOXIDANTS

In many cases different types of inhibitors can be used in a formulation and often shown synergistic effects. For example, in certain formulations a synergistic effect is observed between alkylated diphenylamines and hindered phenolic antioxidants. Initially, aromatic amines react faster with alkyl peroxy radicals than hindered phenols. However, as shown in Figure 14, the hindered phenols act as hydrogen donors for the aminyl radicals regenerating the amine [57, 62]. The hindered phenoxyl radicals then undergo reaction with alkyl peroxy radicals as described above and are eventually consumed. It is only after the hindered phenolic is consumed that the aromatic amine antioxidant begins to be consumed by reaction with alkyl peroxy radical as described above. Thus, in combination, the useful lifetime of the additives

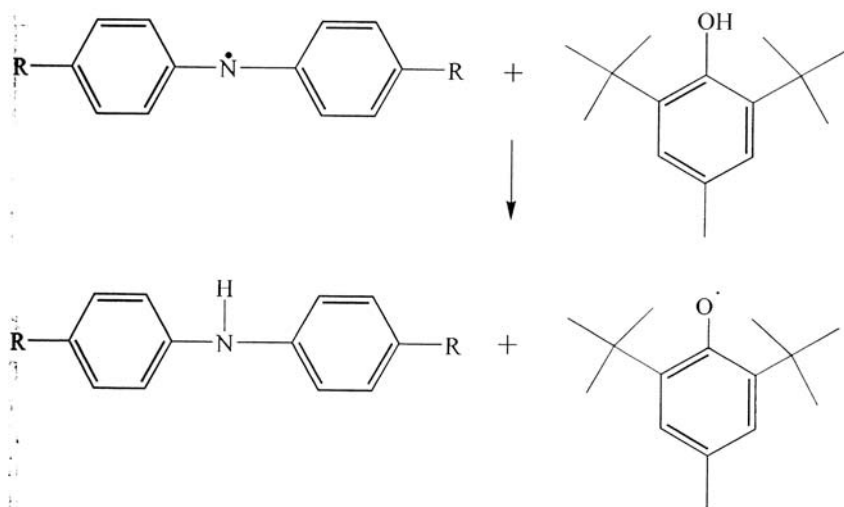


Figure 14. Mechanism of synergism.

is extended beyond the expected performance of each additive if they were used separately.

15 EXPERIMENTAL OBSERVATIONS

The following two examples [68] demonstrate (1) antioxidant behavior that is in agreement with the mechanisms discussed above and (2) how proper antioxidant selection and appropriate combinations can lead to optimized performance. The Turbine Oil Oxidation Test (TOST, ASTM D 943) is run at a relatively low temperature (95°C) with solid-metal catalysts and water present. Figure 15 plots total acid number (TAN) versus time. The test is typically run until a TAN of 2 is exceeded. A turbine oil formulated with an API Group I base stock that contained antioxidant, metal deactivator, and corrosion inhibitor was tested. The alkylated diphenylamine (ADPA) at 0.8 wt% provided protection for about 1800 hr, at which time the ADPA was depleted. The hindered phenolic (HP) at 0.8 wt% provided protection for over 4000 hr, at which time catastrophic failure of the oil occurred. A mixture of ADPA and HP with 0.4 wt% of each additive present provided protection for over 5000 hr, without catastrophic failure. Thus, under these very low-temperature conditions, the HP was superior to the ADPA, but a synergistic mixture of the two additives provided the maximum protection. The rotary bomb oxidation test (RBOT, ASTM D 2272) is run at a high temperature (150°C) with solid-metal catalysts and water present. Figure 16 graphs oxidation induction time in minutes. The test is run until a pressure drop of 25 psi inside the bomb is measured. The pressure drop is due to the rapid and unabated uptake of oxygen by the oil. A turbine oil formulated with an API Group I base stock that contained antioxidant, metal deactivator, and corrosion inhibitor was tested. The alkylated diphenylamine (ADPA) at 0.5 wt% provided protection for about 600 min, at which time the ADPA was depleted. The hindered phenolic (HP) at 0.5 wt% provided protection for over

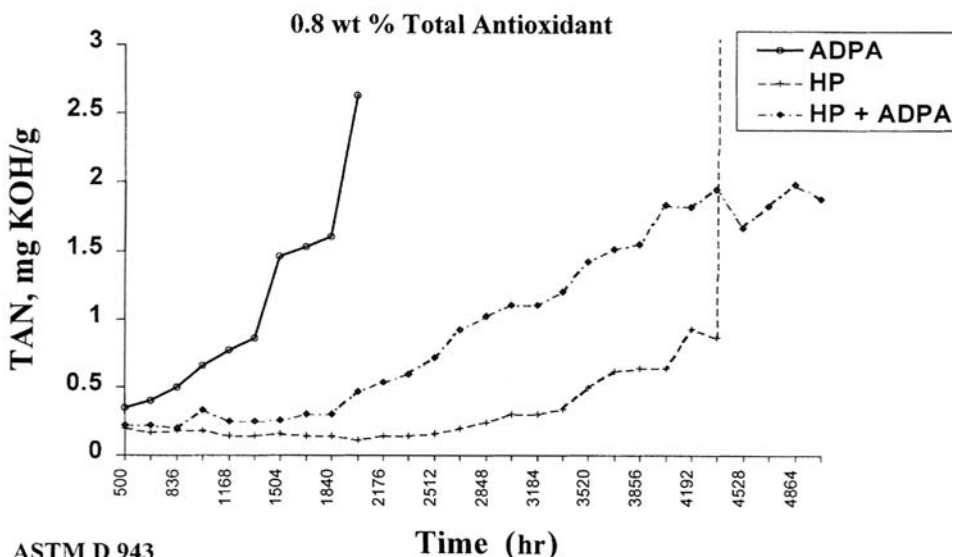


Figure 15. TOST results in turbine oil.

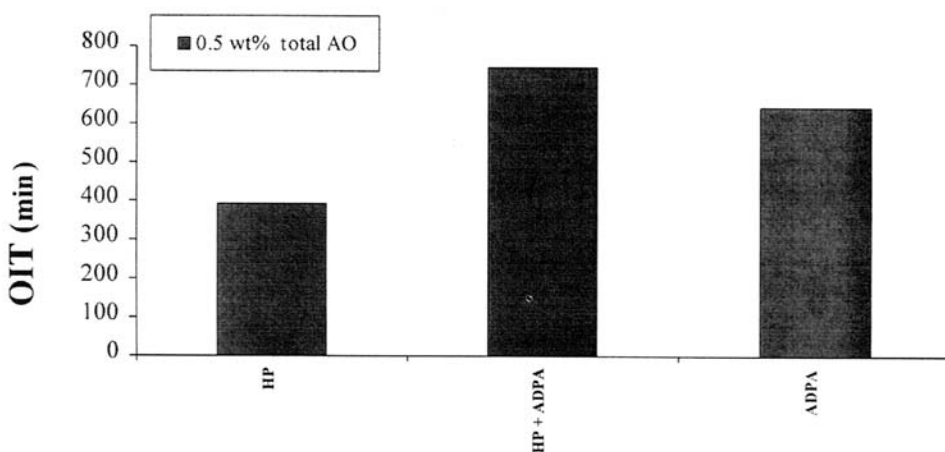


Figure 16. RBOT results in turbine oil.

300 min. Thus, the HP was only half as effective as the ADPA. A mixture of ADPA and HP, with 0.25 wt% of each additive present, provided protection for over 700 min. Therefore, in contrast to the TOST results, under high-temperature conditions the ADPA was superior to the HP, but—just as in the TOST—a synergistic mixture of the two additives provided the maximum protection.

The mechanisms presented support the experimental results and guide the formulator in selection of the proper type of antioxidant(s) for a particular end use. Of course, the formulator in selecting the proper antioxidant(s) must consider these other factors: cost performance, volatility, color, solubility, odor, physical form,

toxicity, and compatibility with other additives. From a pure performance standpoint, hindered phenolics are an excellent primary antioxidant under low-temperature conditions. In contrast, alkylated diphenylamines are an excellent primary antioxidant under high-temperature conditions. Although a synergistic mixture of antioxidants can be used to block multiple oxidation mechanisms, the degree of synergism depends on the formulation, base oil, and test. In fact, several instances of synergy have been identified between sulfur-bearing hindered phenolic and alkylated diphenylamine antioxidants in hydrotreated base stocks [71].

16 ANTIOXIDANT PERFORMANCE WITH BASE STOCK SELECTION

The performance of lubricants is rapidly changing for the better with the development of improved base stocks through processing and synthesis. These improvements are driven by environmental and performance requirements. An area where improvements in the quality of base oils can help includes the need for longer drain intervals, lower volatility, extended warranties, and improved fuel economy.

The conventional base oils (API Group I) are gradually being replaced by a new generation of base oils based on a hydrotreated (hydrocracked) process (API Group II) that provides an oil with low sulfur and a high degree of saturation. A further advance of this refining process combines hydrotreating and hydrocatalytic dewaxing (API Group III), which leads to base oils with a very high viscosity index (VHVI). In fact, these API Group III base oils are a serious challenge to synthetic polyalphaolefins (PAOs) for top-tier oil formulations.

However, without appropriate additive systems, none of the base oil types can meet these requirements. The performance of alkylated diphenylamine and hindered phenolic antioxidants are compared in four base oil categories.

A representative oil from each of the first four API groups was tested [69]; the results are shown in Figure 17. The base oils were tested first without antioxidant

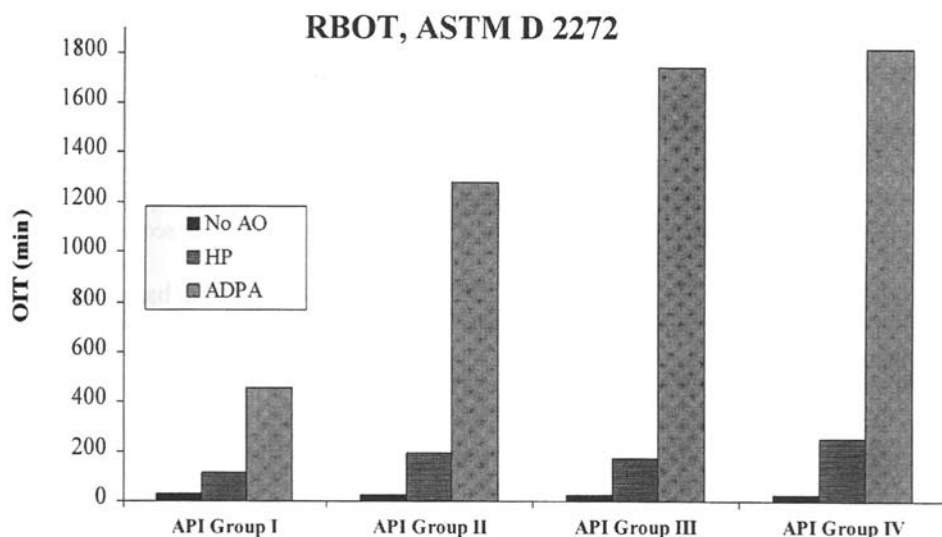


Figure 17. The effect of antioxidants on base oil stability.

Table 1 API Base Oil Categories

API category	Percent saturates	Percent sulfur	Viscosity index
Group I	≤ 90	≥ 0.03	≥ 80 and ≤ 120
Group II	≥ 90	≤ 0.03	≥ 80 and ≤ 120
Group III	≥ 90	≤ 0.03	≥ 120
Polyalphaolefins (PAO)			
Group V	Includes all other base oils not included in the first four groups		

and then with a total antioxidant level of 0.5 wt%. No other additives are present in the formula. The hindered phenolic (HP) antioxidant is 3,5-di-tert-butyl-4-hydroxy-dihydrocinnamic acid, C7–C9 branched alkyl ester, and the alkylated diphenylamine (ADPA) antioxidant is a mixture of butyl, octyl diphenylamines. The results show that the base oils, when tested without antioxidant, perform poorly. When the base oils were tested with the HP antioxidant, they perform modestly, with increasing performance from API Group I to API Group IV. When the base oils were tested with the ADPA antioxidant, their performance is excellent, with increasing performance from API Group I to API Group IV.

17 FUTURE REQUIREMENTS

The need for antioxidants in lubricants will continue, and their volume will increase to meet new performance levels. The key performance changes are environmental in nature: the requirement for better fuel economy, extended drain intervals, and new emission regulations. Radical reformulations of lubricants will be required for use in new engine designs implemented to meet strict emission standards. These standards include lower particulate emissions, NO_x, hydrocarbon, and CO levels. Combining these requirements will increase the performance demands on lubricants, leading to higher levels of antioxidants. To meet these requirements in part, protecting the catalyst from chemical poisoning in emission control devices is being pursued through lower phosphorus and sulfur levels in the oil. This move toward lower phosphorus and sulfur levels (reduction of ZDDP) in next-generation passenger car motor oils is expected to increase the usage for primary as well as secondary antioxidants (as a substitute for ZDDP).

To meet all the performance challenges, improvements in base stocks as well as additives will—and must—continue to take place. Mineral base stocks are being improved to meet these severe performance parameters. The primary method for improving the performance of mineral base stocks consists of hydrotreating these base stocks; this process significantly lowers the natural antioxidants present in lubricants. However, this processing enhances the thermal and oxidation stability of the lubricant when combined with synthetic antioxidants. Therefore, as lubricant formulators increase their use of hydrotreated and synthetic base stocks, the requirements for antioxidants in lubricants is expected to rise. All lubricant components, including base stocks, additives,

and VI improvers, are subject to the aging processes via deterioration through oxidation. The deterioration of lubricants and additives leads to the deposition of sludge and varnish on metal surfaces. Primary antioxidants act to control the propagation of free radicals, which cause the formation of deposits, while secondary antioxidants decompose peroxides. Longer drain intervals for many lubricants will increase antioxidant usage. Slowing the oxidation process enables lubricant life to be extended. Growth in antioxidant usage has been driven by changes in engine designs favoring smaller engines with improved fuel economy. These newer engines operate at higher temperatures than older models. Small increases in the operating temperature of the engine dramatically increase the rate of lubricant oxidation. Therefore, the increased operating temperatures of today's engines require lubricants with higher antioxidant levels. The changing emissions regulations for diesel engines have led to changes in diesel engine design. For example, exhaust gas recirculation (EGR) puts added stress on the lubricant. In order for diesel engine oils to perform in these new engines, under higher temperatures and longer drain intervals, they will also require higher antioxidant levels.

Commercial Antioxidants

<u>Product</u>	<u>Company</u>	<u>Chemical</u>
Additin® 7001	Rhein Chemie	dioctyldiphenylamine
Additin® 7005A	Rhein Chemie	butylated, octylated diphenylamine
Additin® 7010	Rhein Chemie	oligomerized 1,2-dihydro-4-trimethylquinoline
Additin® 7130	Rhein Chemie	phenyl- α -naphthylamine
Additin® 7110	Rhein Chemie	2,6-di- <i>t</i> -butyl- <i>p</i> -cresol
Additin® 7115	Rhein Chemie	phenol derivative sterically hindered
Additin® 7135	Rhein Chemie	styrenated diphenylamine
Additin® 10314A	Rhein Chemie	butylated, octylated diphenylamine
Hitec® 4701	Ethyl	2,6-di- <i>t</i> -butyl phenol
Hitec® 4702	Ethyl	4,4'-methylene bis-(2,6-di- <i>t</i> -butyl phenol)
Hitec® 4703	Ethyl	2,6-di- <i>t</i> -butyl- α -dimethylamino- <i>p</i> -cresol
Hitec® 4720	Ethyl	<i>N,N'</i> -di- <i>sec</i> -butyl- <i>p</i> -phenylenediamine
Hitec® 4721	Ethyl	<i>N,N'</i> -bis(1,4-dimethylpentyl)- <i>p</i> -phenylenediamine
Hitec® 4728	Ethyl	mixture of oligomeric 2,6-di- <i>t</i> -butyl phenols
Hitec® 4733	Ethyl	mixture of 2,6-di- <i>t</i> -butyl phenols
Hitec® 4735	Ethyl	mixture of 2,6-di- <i>t</i> -butyl phenols
Hitec® 4755	Ethyl	boron containing derivatives of Hitec 4702
Hitec® 4777	Ethyl	alkylated diphenylamine
Irganox® L 06	Ciba	octylated PANA
Irganox® L 57	Ciba	butylated, octylated diphenylamine

Irganox® L 67	Ciba	dinonyl diphenylamine
Irganox® L 109	Ciba	hindered bis-phenolic
Irganox® L 118	Ciba	liquid hindered phenolic with thioether
Irganox® 135	Ciba	liquid hindered phenolic
Irganox® E 201	Ciba	liquid di- α -tocopherol (Vitamin E)
Irgaphos® 168	Ciba	tri-(di- <i>t</i> -butylphenyl) phosphite
Irganox® 1010	Ciba	high-MW hindered phenolic
Irganox® 1035	Ciba	high-MW hindered bis-phenolic with thioether
Irganox® 1076	Ciba	high-MW hindered phenolic
Naugard® BHT	Crompton	2,6-di- <i>t</i> -butyl- <i>p</i> -cresol
Naugalube® 531	Crompton	3,5-di- <i>t</i> -butyl-4-hydroxy-hydrodnamic acid, C ₇ -C ₉ branched alkyl ester
Naugalube® 438	Crompton	dioctyl diphenylamine
Naugalube® 438L	Crompton	dinonyl diphenylamine
Naugalube® 635	Crompton	styrenated diphenylamine
Naugalube® 640	Crompton	butylated, octylated diphenylamine
Naugalube® 680	Crompton	octylated, styrenated diphenylamine
Naugalube® AMS	Crompton	α -methystyrenated DPA
Naugalube® APAN	Crompton	alkylated PANA
Naugard® PANA	Crompton	phenyl- α -naphthylamine
Naugalube® TMQ	Crompton	oligomerized 1,2-dihydro-4-trimethyl quinoline
Naugalube® 403	Crompton	<i>N</i> - <i>N'</i> -di- <i>sec</i> -butyl- <i>p</i> -phenylenediamine
Naugalube® 410	Crompton	<i>N</i> -phenyl- <i>N'</i> -isopropyl- <i>p</i> -phenylenediamine
Naugalube® 420	Crompton	<i>N</i> -phenyl- <i>N'</i> -alkyl- <i>p</i> -phenylenediamine
Vanlube® DND	RT Vanderbilt	dinonyl diphenylamine
Vanlube® NA	RT Vanderbilt	nonylated, ethylated diphenylamine
Vanlube® PCX	RT Vanderbilt	2,6-di- <i>t</i> -butyl- <i>p</i> -cresol
Vanlube® PNA	RT Vanderbilt	alkylated PANA
Vanlube® RD	RT Vanderbilt	oligomerized 1,2-dihydro-4-trimethyquinoline
Vanlube® SL	RT Vanderbilt	octylated, styrenated diphenylamine
Vanlube® SS	RT Vanderbilt	octylated diphenylamine
Vanlube® 81	RT Vanderbilt	dioctyl diphenylamine
Vanlube® 848	RT Vanderbilt	butylated, octylated DPA
Vanlube® 849	RT Vanderbilt	α methyl styrenated DPA
Vanlube® 881-P	RT Vanderbilt	2,5-dimercapto-1,3,4-thiadiazole derivative
Vanlube® 887	RT Vanderbilt	tolutriazole compound in oil
Vanlube® 887E	RT Vanderbilt	tolutriazole compound in ester

Commercial Metal Deactivators

Hitec® 4708	Ethyl	<i>N,N''</i> -disalicylidene-1,2-diaminopropane
Irgamet® 30	Ciba	triazole derivative
Irgamet® 39	Ciba	tolutriazole derivative

Irgamet® 42	Ciba	water-soluble toluotriazole derivative
Vanlube® 691-C	RT Vanderbilt	proprietary blend
Vanlube® 704	RT Vanderbilt	proprietary blend

REFERENCES

1. J Baird. Great Britain Patent 1516 (1872).
2. F Haas. Lubricant. U.S. Patent 2,162,398 (6/13/39, Archer-Daniels-Midland Co.).
- 3a. WH Kobbe. Sulphur-containing oil composition and method of making the same. U.S. Patent 1,844,400(2/9/32).
- 3b. RC Palmer, PO Powers. Sulphurized terpene oil and process of preparing the same. U.S. Patent 1,926,687 (9/12/33, Newport Industries, Inc.).
- 3c. EC Knowles, FC McCoy, JA Patterson. Lubricating oil and method of lubricating. U.S. Patent 2,417,305 (3/11/47, The Texas Co.).
- 4a. BH Lincoln, WL Steiner, GD Byrkit. Sulphur containing lubricant. U.S. Patent 2,218,132 (10/15/40, Continental Oil Co.).
- 4b. BH Lincoln, WL Steiner, GD Byrkit. Sulphur containing lubricant. U.S. Patent 2,313,248 (3/9/43, The Lubri-Zol Development Corp.).
- 4c. BH Lincoln, GD Byrkit, WL Steiner. Method for the synthesis of sulphur-bearing derivatives of high molecular weight. U.S. Patent 2,348,080 (5/2/44, Continental Oil Co.).
- 4d. BB Farrington, VM Kostainsek, GH Denison, Jr. Compounded lubricant. U.S. Patent 2,346,156 (4/11/44, Standard Oil Co. of California).
- 5a. LA Mikeska, E Lieber. Preparation of phenol sulfides. U.S. Patent 2,139,321 (12/6/38, Standard Oil Development Co.).
- 5b. LA Mikeska, CA Cohen. Mineral oil stabilizing agent and composition containing same. U.S. Patent 2,139,766 (12/13/38, Standard Oil Development Co.).
- 5c. LA Mikeska, E Lieber. Stabilized lubricating composition. U.S. Patent 2,174,248 (9/26/39, Standard Oil Development Co.).
- 5d. LA Mikeska, E Lieber. Polymerization and condensation products. U.S. Patent 2,239,534 (4/22/41, Standard Oil Development Co.).
- 5e. RW Richardson. Oxidation inhibitor. U.S. Patent 2,259,861 (10/21/41, Standard Oil Development Co.).
6. HF Askew, GJJ Jayne, JS Elliott. Lubricant compositions. U.S. Patent 3,882,031 (5/6/75, Edwin Cooper & Co. Ltd.).
7. JR Spence. Lubricating compositions containing normal-alkyl substituted 2-thiazoline disulfide antioxidants. U.S. Patent 4,485,022 (11/27/84, Phillips Petroleum Co.).
8. MF Salomon. Antioxidant compositions. U.S. Patent 4,764,299 (8/16/88, The Lubri-zol Corp.).
9. H Oumar-Mahamat, AG Horodysky, A Jeng. Dihydrobenzothiophenes as antioxidant and antiwear additives for lubricating oils. U.S. Patent 5,514,289 (5/7/96, Mobil Oil Corp.).
10. AL Brown. Treatmetn of hydrocarbon oils. U.S. Patent 1,234,862 (7/31/17, Westing-house and Electric Manufacturing Co.).
- 11a. RC Moran, WL Evers, EW Fuller. Petroleum product and method of making same,. U.S. Patent 2,058,343 (10/20/36, Socony-Vacuum Oil Co., Inc.).
- 11b. RC Moran, AP Kozacik. Mineral oil composition. U.S. Patent 2,151,300 (3/21/39, Socony-Vacuum Oil Co., Inc.).
- 12a. HV Ashburn. WG Alsop. Lubricating oil. U.S. Patent 2,221,162 (11/12/40, The Texas Co.).
- 12b. FW Hall, CG Towne. Method of lubrication. U.S. Patent 2,257,601 (9/30/41, The Texas Co.)

- 12c. S Musher. Lubricating oil and the method of making the same. U.S. Patent 2,223,941 (12/3/40, The Musher Foundation).
- 12d. CM Loane, JW Gaynor. Lubricant. U.S. Patent 2,322,859 (6/29/43, Standard Oil Co.).
- 13a. BB Farrington, JO Clayton. Compounded mineral oil. U.S. Patent 2,228,658 (1/14/41, Standard Oil Co. of California).
- 13b. BB Farrington, JO Clayton, JT Rutherford. Compounded mineral oil. U.S. Patent 2,228,659 (1/14/41, Standard Oil Co. of California).
- 14a. JT Rutherford, RJ Miller. Compounded hydrocarbon oil. U.S. Patent 2,252,984 (8/19/41, Standard Oil Co. of California).
- 14b. JT Rutherford, RJ Miller. Compounded oil. U.S. Patent 2,252,985 (8/19/41, Standard Oil Co. of California).
- 14c. PA Asseff. Lubricant. U.S. Patent 2,261,047 (10/28/41, The Lubri-Zol Corp.).
- 14d. EW Cook, WD Thomas, Jr. Crankcase lubricant and chemical compound therefore. U.S. Patent 2,342,572 (2/22/44, American Cyanamid Co.).
- 14e. EW Cook, WD Thomas, Jr. Crankcase lubricant and chemical compound therefore. U.S. Patent 2,344,392 (3/14/44, American Cyanamid Co.).
- 14f. EW Cook, WD Thomas, Jr. Lubricating oil composition. U.S. Patent 2,344,393 (3/14/44, American Cyanamid Co.).
- 14g. EW Cook, WD Thomas, Jr. Lubricating composition. U.S. Patent 2,358,305 (9/19/44, American Cyanamid Co.).
- 14h. EW Cook, WD Thomas, Jr. Lubricating compositions. U.S. Patent 2,368,000 (1/23/45, American Cyanamid Co.).
- 15a. LL Davis, BH Lincoln, GD Byrkit. Method of synthesizing sulphur-bearing high molecular weight hydrocarbons. U.S. Patent 2,278,719 (4/7/42, Continental Oil Co.).
- 15b. CD Kelson. Phosphorus sulphide-hydrocarbon reaction product. U.S. Patent 2,315,529 (4/6/43, Standard Oil Co.).
- 15c. CM Loane, JW Gaynor. Lubricant. U.S. Patent 2,316,078 (4/6/43, Standard Oil Co.).
- 15d. CN White. Lubricant. U.S. Patent 2,316,091 (4/6/43, Standard Oil Co.).
- 15e. RL May. Reaction products of aliphatic alcohols and terepene-phosphorus sulphide. U.S. Patent 2,356,073 (8/15/44, Sinclair Refining Co.).
- 15f. RL May. Zinc salt of the reaction products of aliphatic alcohols and terepene-phosphorus sulphide. U.S. Patent 2,356,074 (8/15/44, Sinclair Refining Co.).
- 15g. JM Musselman, HP Lankelma. Preparation of compounds for lubricants, etc. U.S. Patent 2,357,346 (9/5/44, The Standard Oil Co.).
- 15h. HG Berger, TT Noland, EW Fuller. Mineral oil composition. U.S. Patent 2,373,094 (4/10/45, Socony-Vacuum Oil Co.).
- 15i. LW Mixon. Interface modifier. U.S. Patent 2,375,315 (5/8/45, Standard Oil Co.).
- 15j. LW Mixon, CM Loane. Lubricant. U.S. Patent 2,377,955 (6/8/45, Standard Oil Co.).
- 15k. RL May. Reaction products of alkylated phenols and terepene-phosphorus sulphide. U.S. Patent 2,379,312 (6/26/45, Sinclair Refining Co.).
- 15l. TT Noland. Mineral oil composition. U.S. Patent 2,379,453 (7/3/45, Socony-Vacuum Oil Co.).
- 15m. EC Hughes, WE Scovill. Mineral oil beneficiation. U.S. Patent 2,381,907 (8/14/45, The Standard Oil Co.).
- 15n. RL May. Lubricant. U.S. Patent 2,392,252 (1/1/46, Sinclair Refining Co.).
- 15o. RL May. Lubricant. U.S. Patent 2,392,253 (1/1/46, Sinclair Refining Co.).
- 15p. JM Musselman, HP Lankelma. Lubricants. U.S. Patent 2,396,719 (3/19/46, The Standard Oil Co.).
- 15q. JD Bartleson. Additives for lubricants. U.S. Patent 2,403,894 (7/9/46, The Standard Oil Co.).
- 15r. RL May. Lubricating oil. U.S. Patent 2,409,877 (10/22/46, Sinclair Refining Co.).
- 15s. BH Lincoln, GD Byrkit. Lubricating oil. U.S. Patent 2,415,296 (2/4/47).

- 15t. HG Berger, EW Fuller. Mineral oil composition. U.S. Patent 2,416,281 (2/25/47, Socony-Vacuum Oil Co.).
- 15u. TH Rogers, RW Watson, JW Starrett. Lubricant. U.S. Patent 2,422,585 (6/17/47, Standard Oil Co.).
- 15v. EW Fuller, and HS Angel. Mineral oil composition. U.S. Patent 2,455,668 (12/7/48, Socony-Vacuum Oil Co.).
16. DL Clason, CW Schroeck. Phosphite treatment of phosphorus acid salts and compositions produced thereby. U.S. Patent 4,263,150 (4/21/81, The Lubrizol Corp.).
17. G Rivier. Novel metallic dithiophosphates and their use as additives for lubricating oils. U.S. Patent 4,288,335 (9/8/81, Orogil).
18. CW Schroeck. Metal salts of lower dialkylphosphorodithioic acids. U.S. Patent 4,466,895 (8/21/84, The Lubrizol Corp.).
19. DL Clason, CW Schroeck. Mixed metal salts and lubricants and functional fluids containing them. U.S. Patent 4,308,154 (12/29/81, The Lubrizol Corp.).
20. SA Levine. RC Schlicht, H Chafetz, JR Whiteman. Molybdenum derivatives and lubricants containing same. U.S. Patent 4,428,848 (1/31/84, Texaco, Inc.).
- 21a. L de Vries, JM King. Process of preparing molybdenum complexes, the complexes so-produced and lubricants containing same. U.S. Patent 4,263,152 (4/21/81, Chevron Research Co.).
- 21b. L de Vries, JM King. Process of preparing molybdenum complexes, the complexes so-produced and lubricants containing same. U.S. Patent 4,265,773 (5/5/81, Chevron Research Co.).
22. L de Vries, JM King. Antioxidant combinations of molybdenum complexes and aromatic amine compounds. U.S. Patent 4,370,246 (1/25/83, Chevron Research Co.).
23. H Shaub. Mixed antioxidant composition. Eur. Patent 719313B1 (8/6/97, Exxon Chemical Patents, Inc.).
24. K Arai, H Tomizawa. Lubricating oil composition. U.S. Patent 5,605,880 (2/25/97, Exxon Chemical Patents, Inc.).
25. H Tomizawa. Lubricating oil composition for internal combustion engines. U.S. Patent 5,688,748 (11/18/97, Tonen Corp.).
26. VJ Gatto. Antioxidant system for lubrication base oils. U.S. Patent 5,840,672 (11/24/98, Ethyl Corp.).
- 27a. VJ Gatto, MT Devlin. Lubricant containing molybdenum compound and secondary diarylamine. U.S. Patent 5,650,381 (7/22/97, Ethyl Corp.).
- 27b. VJ Gatto, MT Devlin. Lubricating composition. Great Britain Patent Appl. 2,307,245 (5/21/97, Ethyl Corp.).
28. TE Nalesnik, CA Migdal. Oil-soluble molybdenum multifunctional friction modifier additives for lubricant compositions. U.S. Patent 6,103,674 (8/15/00, Uniroyal Chemical Company, Inc.).
- 29a. TH Rogers. Refined viscous hydrocarbon oil. U.S. Patent 1,774,845 (9/2/30, Standard Oil Co.).
- 29b. TH Rogers. Refined viscous hydrocarbon oil. U.S. Patent 1,793,134 (2/17/31, Standard Oil Co.).
30. EN Roberts. Lubricant. U.S. Patent 2,409,799 (10/22/46, Standard Oil Co.).
31. VN Jenkins. Diesel engine lubricating oil. U.S. Patent 2,366,191 (1/2/45, Union Oil Co. of California).
32. WE Wright Antioxidant diamine. U.S. Patent 4,456,541 (6/26/84, Ethyl Corp.).
33. BK Bandlish, FC Loveless, W Nudenberg. Amino compounds and use of amino compounds as antioxidants in lubricating oils. Eur. Patent 022281B1 (9/14/83, Uniroyal, Inc.).
34. R Muller, W Hartmann. *N,N'*-Diphenyl-*p*-phenylenediamines, method for their production and their use as stabilizers for organic materials. Eur. Patent Appl. 072575A1 (2/23/83, Chemische Werke Lowi GmbH).

35. RF Malherbe. 2,3-Dihydroperimidines as antioxidants for lubricants. U.S. Patent 4,389,321 (6/21/83, Ciba-Geigy Corp.).
- 36a. JT Roberts. *N,N'*-Disubstituted 2,4'-diaminodiphenyl ethers as antioxidants, U.S. Patent 4,309,294 (1/5/82, UOP, Inc.).
- 36b. JT Roberts. Imines of 2,4-diaminodiphenyl ethers as antioxidants for lubricating oils and greases. U.S. Patent 4,378,298 (3/29/83, UOP, Inc.).
37. RL Sung, BH Zoleski. Diesel lubricant composition containing 5-amino-triazole-succinic anhydride reaction product. U.S. Patent 4,256,595 (3/17/81, Texaco, Inc.).
38. JT Lai. Synthetic lubricant antioxidant from monosubstituted diphenylamines. U.S. Patent 5,489,711 (2/6/96, The B.F. Goodrich Co.).
39. JT Lai, DS Filla. Process for production of liquid alkylated diphenylamine antioxidant. U.S. Patent 5,750,787 (5/12/98, The B.F. Goodrich Co.).
- 40a. M Braid. Lubricant compositions containing *N*-tertiary alkyl benzotriazoles. U.S. Patent 4,519,928 (5/28/85, Mobil Oil Corp.).
- 40b. J Shim. Lubricant compositions containing antioxidant mixtures comprising substituted thiazoles and substituted thiadiazole compounds. U.S. Patent 4,260,501 (4/7/81, Mobil Oil Corp.).
- 41a. J Shim. Multifunctional additives. U.S. Patent 4,511,481 (4/16/85, Mobil Oil Corp.).
- 41b. J Shim. Triazole-dithiophosphate reaction product and lubricant compositions containing same. U.S. Patent 4,456,539 (6/26/84, Mobil Oil Corp.).
42. HJ Andress, Jr., RH Davis. Arylamine-aldehyde lubricant antioxidants. Eur. Patent Appl. 083871A2 (7/20/83, Mobil Oil Corp.).
43. JM Cohen. Oxidatively coupled hydroxyaromatic compounds and fuels and lubricants containing them. U.S. Patent 4,256,596 (3/17/81, The Lubrizol Corp.).
44. M Braid. Phenolic antioxidants and lubricants containing same. U.S. Patent 4,551,259 (11/5/85, Mobil Oil Corp.).
45. BG McKinnie, PF Ranken. (Hydrocarbylthio)phenols and their preparation. U.S. Patent 4,533,753 (8/6/85, Ethyl Corp.).
46. VJ Gatto. Hydroxyphenyl-substituted amine antioxidants. U.S. Patent 5,292,956 (3/8/94, Ethyl Corp.).
47. WY Lam, VJ Gatto. Sulfurized phenolic antioxidant compositions, method of preparing them, and petroleum products containing them. Eur. Patent Appl. 0811631A2 (12/10/97, Ethyl Corp.).
48. H Oumar-Mahamat. AG Horodysky. Phenolic imidazoline antioxidants. U.S. Patent 5,846,917 (12/8/98, Mobil Oil Corp.).
49. MF Salomon. *N*-Substituted thio alkyl phenothiazine. U.S. Patent 5,034,019 (7/23/91, The Lubrizol Corp.).
50. L Germanaud, P Azorin, P Turello. Antioxidant nitrogen-containing additives for lubricating oils. Fr. Patent 2,639,956 (6/8/90, Elf France).
51. MM Kapuscinski, RT Biggs. Dispersant and antioxidant VI improver based on olefin copolymers containing phenothiazine and aromatic amine groups. U.S. Patent 5,942,0471 (8/24/99, Ethyl Corp.).
52. H Camenzind, A Dratva, P Hanggi. Ash-free and phosphorus-free antioxidants and antiwear additives for lubricants. Eur. Patent Appl. 894,793 (2/3/99, Ciba Specialty Chemicals Holding, Inc.).
- 53a. FB Downing, HM Fitch. Lubricant. U.S. Patent 2,343,756 (3/7/44, E.I. du Pont de Nemours & Co.).
- 53b. AL Fox. Solution of copper mercaptides from terpenes. U.S. Patent 2,349,820 (5/30/44, E.I du Pont de Nemours & Co.).
- 53c. FB Downing, HM Fitch. Lubricating oil. U.S. Patent 2,356,661 (8/22/44, E.I. du Pont de Nemours & Co.).

54. T Colclough, FA Gibson, JF Marsh. Lubricating oil compositions containing ashless dispersant, zinc dihydrocarbyldithiophosphate, metal detergent and a copper compound. U.S. Patent 4,867,890 (9/19/89).
55. A Gurierrez, DW Brownawell, SJ Brois. Copper complexes of oxazolines and lactone oxazolines as lubricating oil additives. U.S. Patent 4,486,326 (12/4/84, Exxon Research & Engineering Co.).
56. TR Hopkins. Copper salts of succinic anhydride derivatives. U.S. Patent 4,552,677 (11/12/85, The Lubrizol Corp.).
57. M Rasberger. Oxidative degradation and stabilization of mineral oil based lubricants in: RM Motier and ST Orszulik, eds. *Chemistry and Technology of Lubricants*. London:Blackie Academic & Professional, 1997, pp 98–143.
58. PR Paolino. Antioxidants in JT Lutz, Jr., ed. *Thermoplastic Polymer Additives*. New York:Marcel Dekker, 1989, pp 1–35.
59. T Colclough. *Ind Eng Chem Res* 26:1888–1895, 1987.
60. X Maleville, D Faure, A Legros, JC Hipeaux. *Lubrication Science* 9:3–60, 1996.
61. EB Boozer, GS Hammond, CE Hamilton, JN Sen. *J Am Chem Soc* 77:3233–3237, 1955.
62. J Pospisil. *Advances in Polymer Science* 124:87–190, 1995.
63. RK Jensen, S Korcek, M Zinbo, JL Gerlock. *J Org Chem* 60:5396–5400, 1995.
64. J Pospisil. *Polymer Degradation and Stability* 20:181–202, 1988.
65. H Berger, TAB Bolsman, DM Brouwer. In *Developments in Polymer Stabilisation*. Vol. 6 G Scott, ed. London:Elsevier Applied Science Publishers, 1983, pp 1–27.
66. RK Jensen, S Korcek, LR Mahoney, M Zinbo. *J Am Chem Soc* 101:7574–7584, 1979.
67. PC Hamblin, D Chasan, U Kristen. A review: ashless antioxidants, copper deactivators and corrosion inhibitors. Their use in lubricating oils in J Bartz, ed. *5th International Colloquium on Additives for Operational Fluids*. Technische Akademie Esslingen, 1986.
68. CA Migdal. *Proceedings of the 4th Annual Fuels & Lubes Asia Conference*, V Villena-Denton, ed. Fuels & Lubes Asia Publications, Inc., 1998, p 11–1.
69. CA Migdal. *Proceedings of the 5th Annual Fuels & Lubes Asia Conference*, V Villena-Denton, ed. Fuels & Lubes Asia Publications, Inc., 1999.
70. T Colclough. *Ind Eng Chem Res* 26:1888–1895, 1987.
71. VJ Gatto, MA Grina. *Lubrication Engineering* 11–20, 1999.
72. JL Reyes-Gavilan, P Odorisio. *NLGI Spokesman* 64(11):22–33, 2001.

2

Zinc Dithiophosphates

RANDOLPH A. McDONALD

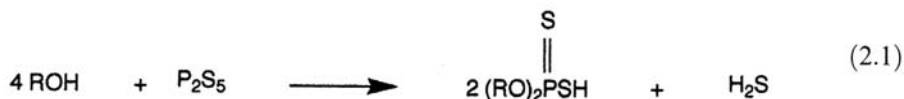
Functional Products, Inc., Macedonia, Ohio, U.S.A.

1 INTRODUCTION

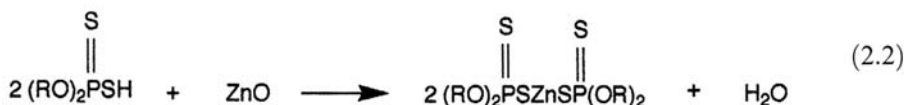
Zinc dialkyldithiophosphates (ZDDP) have been used for over 50 years in the lubricant industry as low-cost, multifunctional additives in engine oils, transmission fluids, hydraulic fluids, gear oils, greases, and other lubricant applications. The power of this particular compound is in its ability to simultaneously function as an excellent antiwear agent, a mild extreme-pressure (EP) agent, and an effective oxidation and corrosion inhibitor, all at a very low cost in comparison to the alternate chemistries available on the market. This is why it is still manufactured on a large scale by such companies as the ExxonMobil Corporation, Chevron Corporation, Ethyl Corporation, Lubrizol Corporation, and others. To date, as much as 300 million lb of ZDDP are still manufactured annually in the industrialized West.

2 SYNTHESIS AND MANUFACTURE

Zinc dialkyldithiophosphate was first patented on December 5, 1944, by Herbert C. Freuler of the Union Oil Company of California in Los Angeles [1]. The multifunctionality of ZDDP was immediately noticed as Freuler indicated a noticeable increase in both the oxidation and corrosion resistance of the lubricants tested with the novel compound at a 0.1–1.0% treatment level. The initial synthesis Freuler carried out involved the reaction of four moles of alcohol with one mole of phosphorus pentasulfide to produce two moles of the intermediate dialkyldithiophosphate acid and one mole of hydrogen sulfide:



followed by neutralization of the acid with one mole of zinc oxide:



This same synthetic route is still used today in the manufacture of zinc dialkyldithiophosphate. The P_2S_5 , a flammable solid produced from the high-temperature reaction between elemental sulfur and phosphorus, is provided to the ZDDP manufacture in sealed aluminum bins containing from 500 to 7200 lb P_2S_5 . The P_2S_5 is hopped into the reactor containing the alcohol under a blanket of nitrogen. This is due to the ignitability of both the alcohol and P_2S_5 when exposed to air. The hydrogen sulfide byproduct, a highly toxic gas, is either converted to sodium sulfide solution in a caustic scrubber or thermally oxidized to sulfur dioxide. The heat of reaction and rate of hydrogen sulfide evolution are controlled by the addition rate of the P_2S_5 as well as the flow rate of the cooling water. The acid is then neutralized by the zinc oxide; the reaction temperature is controlled by the addition rate of either reactant depending on whether it is an acid to oxide, or oxide to acid, addition scheme. Enough zinc oxide is used to neutralize the acid to a pH range that will give a product suitably stable to thermal degradation, hydrolysis, and hydrogen sulfide evolution. The water formed from the reaction and the residual alcohol is vacuum-distilled. Any unreacted zinc oxide is then filtered, requiring a filtration system capable of removing particles as small as 0.1–0.8 micron. A larger molar excess of zinc oxide is often necessary to obtain the pH required for stability. The various manufacturers have done much work to reduce the amount of zinc oxide used to obtain product stability (such as the addition of low-molecular-weight alcohols or carboxylic acids to lower the amount of residual sediment in the product prior to filtration) [2]. The filtered, liquid product, with or without additional petroleum oil, is then provided to the customer in drums or in bulk.

3 CHEMICAL AND PHYSICAL NATURE

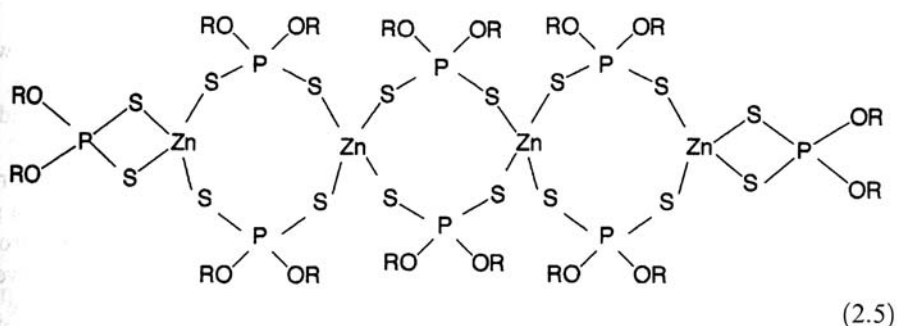
Zinc dialkyldithiophosphate is an organometallic compound having four sulfur atoms coordinated to one zinc atom, which is in a tetrahedral, sp^3 hybridized state. A Raman spectrum of ZDDP shows a strong P-S symmetric stretching band near 540 cm^{-1} and the absence of a strong Raman band near 660 cm^{-1} indicating a symmetrical sulfur-zinc coordination arrangement as in structure (2.3):



versus structure (2.4):



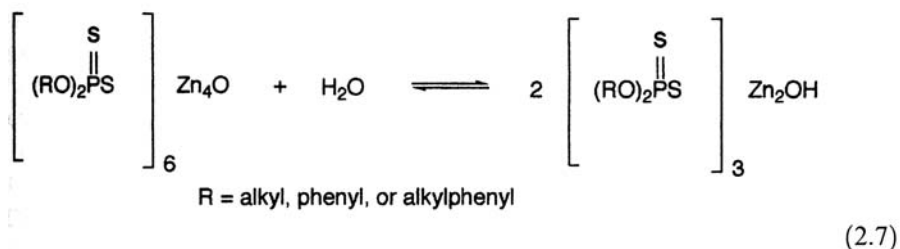
often given in the literature. The strong IR band at 600 cm^{-1} pointing to $\text{P}=\text{S}$ stretching would be more consistent with PS_2 antisymmetrical stretching in light of the Raman spectrum [3]. The neutral ZDDP molecules as represented in structure (3.1) actually exist as monomer, dimer, trimer, or oligomer depending on the state of the ZDDP, crystalline or liquid, the concentration of ZDDP in solvent, and the presence of additional compounds. The proposed structure for a tetramer in the case of a neutral zinc diisobutyldithiophosphate in hexane as determined by dynamic light scattering is shown in structure (2.5) [4]:



Under overbased conditions, when the ratio of dialkyldithiophosphate acid to zinc oxide is less than 2:1, a basic zinc salt (2.6):



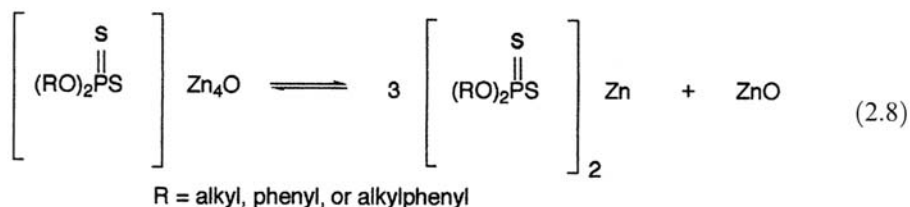
will be synthesized along with the neutral salt. The basic salt is a tetrahedron of zinc atoms surrounding a central oxygen atom with $(\text{RO})_2\text{PS}_2$ ligands along each edge of the tetrahedron. Crystallographic analysis of pure basic zinc salts have established the near equivalency of $\text{P}-\text{S}-\text{Zn}$ bonds. Raman spectra have also shown symmetrical $\text{P}-\text{S}$ stretching, supporting a symmetrical sulfur-zinc coordination arrangement for the basic ZDDPs [3]. In the presence of water, as one would encounter during



commercial ZDDP manufacture, the basic zinc salt will be in equilibrium with the basic zinc double salt as seen in (2.7):

The stoichiometric excess of zinc oxide used in commercial ZDDP manufacture gives rise to a mixture of basic zinc salt (or zinc double salt) and neutral salt, the ratio depending on the amount of excess zinc oxide used and the molecular weight of the alkyl groups involved, where short alkyl groups tend to promote the formation

of more basic zinc salt. Some researchers have postulated the existence of an equilibrium between the basic and the neutral salt as seen in (2.8):



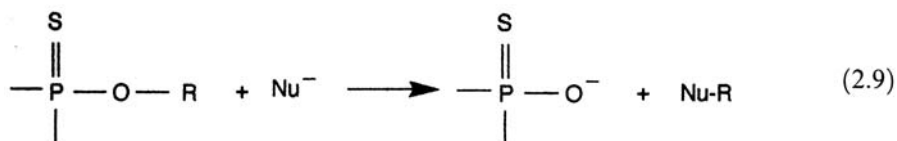
but performance differences seen between the two salts with respect to wear would imply that a more complex situation may exist [5]. As reported in the literature, basic ZDDP salts spontaneously decompose in solution into neutral complexes and zinc oxide when the temperature is increased [6].

Pure zinc dialkyldithiophosphates, with alkyl groups of four carbons or less, are solid at ambient temperatures (with the exception of sec-butyl, which is a semi-solid at room temperature) and tend to have limited or no solubility in petroleum base stocks. Zinc dialkyldithiophosphates with aryl or alkyl groups above five carbons are liquid at ambient temperature. To utilize the less expensive and more readily available low-molecular-weight alcohols and yet produce oil-soluble products, commercial manufactures use mixtures of high-molecular-weight (i.e., higher than four carbons) and low-molecular-weight alcohols to obtain a statistical distribution of products favoring lesser amounts of pure low-molecular-weight ZDDPs. Other methods have also been developed to increase the amount of lower-molecular-weight alcohols in ZDDPs. These include the addition of ammonium carboxylates to inhibit precipitation [7] and the use of alkyl succinimides as solubilizing-complexing agents [8].

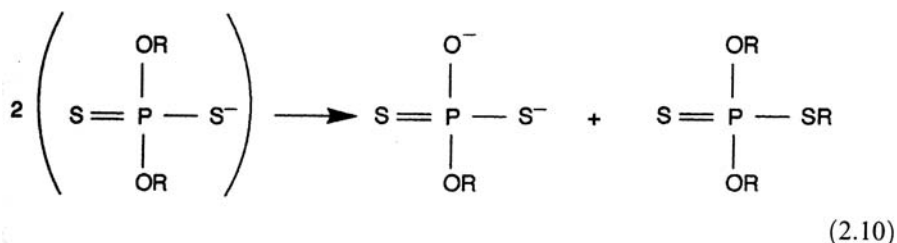
4 THERMAL AND HYDROLYTIC STABILITY

The study of the thermal degradation of ZDDP is important in that much of the tribological characteristics of ZDDP can be explained by the effects of its decomposition products. The thermal decomposition of ZDDP in mineral oil has been found to be extremely complex. A zinc dialkyldithiophosphate in oil, upon heating to degradation, will give off volatile compounds such as olefin, alkyl disulfide, and alkyl mercaptan. A white precipitate will also form that been determined to be a low sulfur containing zinc pyrophosphate. The oil phase will contain varying amounts of S,S,S-trialkyltetra-thiophosphate, O,S,S-trialkyltrithiophosphate, and O,O,S-trialkyldithiophosphate depending on the alkyl chain and the extent of degradation. The decomposition products of ZDDPs made from secondary alkyl alcohols, straight-chain primary alkyl alcohols, and branched primary alkyl alcohols appear similar in content but differ in proportions. This implies a similar mechanism for both primary and secondary ZDDP decomposition.

O-alkyl thiophosphate esters are powerful alkylating agents. The P-O-R group is susceptible to nucleophilic attack, thus producing an alkylated nucleophile and thiophosphate anion. The incoming nucleophile initiates the reaction by an attack on the alpha carbon. This shows a kinetic dependence upon alkyl structure(2.9):



Steric hindrance to the approach of the nucleophile will play a large rate-controlling factor here. The only nucleophile initially present is the dithiophosphate itself. The decomposition is initiated by one dithiophosphate anion attacking another, possibly on the same zinc atom (2.10):



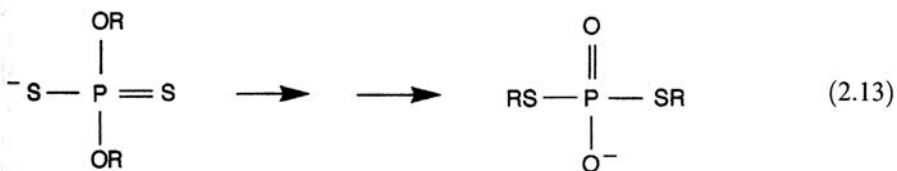
The resulting di-anion then attacks the triester, producing O,S-dialkyldithiophosphate anion (2.11):



resulting in a migration of an alkyl group from oxygen to sulfur. This anion then, in a route analogous to the dialkyldithiophosphate anion, reacts with itself in a nucleophilic attack to effect another alkyl transfer from oxygen to sulfur producing O,S,S-trialkyldithiophosphate (2.12):

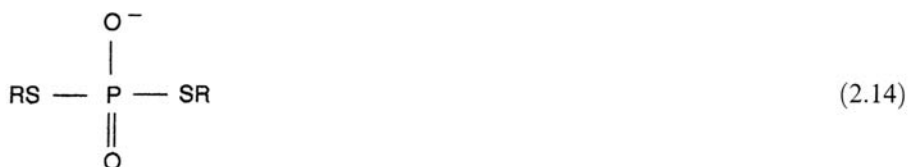


The net effect of the above reactions is a double alkyl migration from oxygen to sulfur (2.13):

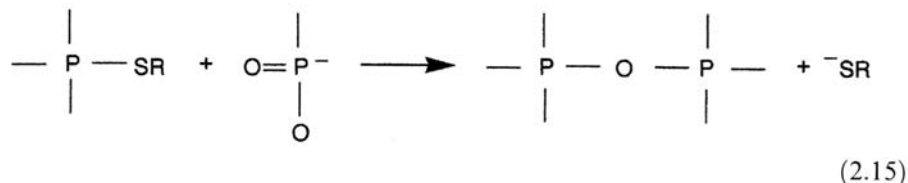


The major gases associated with ZDDP decomposition are dialkylsulfide (RSR), alkyl mercaptan (RSH), and olefin. The relative amounts of each depend on whether the alkyl group in the ZDDP is primary, branched primary, or secondary [9]. In the presence of mercaptide anion (RS⁻) from the intermediate zinc mercaptide

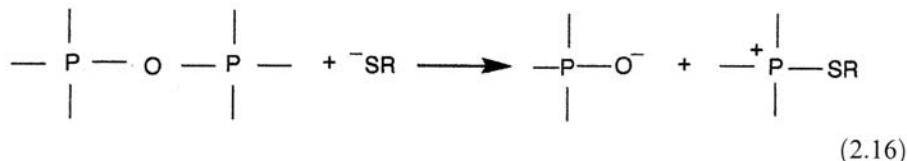
(Zn(RS)₂, O,S,S-trialkylldithiophosphate will react with mercaptide to produce alkyl mercaptan and structure (2.14):



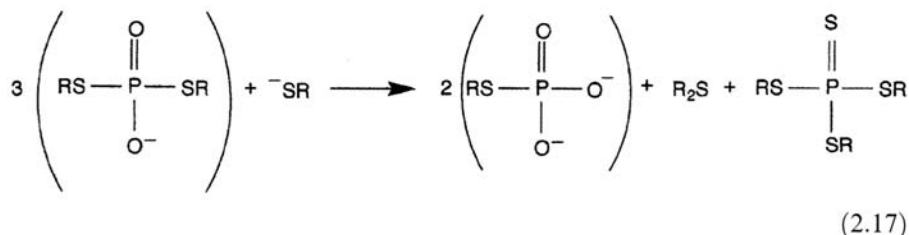
The nucleophilic phosphoryl oxygen (P=O) will then attack another phosphorus atom to produce a P-O-P bond as in (2.15):



A mercaptide anion subsequently cleaves the P-O-P bond at the original P-O site, giving rise to a net exchange of one atom of oxygen for one atom of sulfur between the two phosphorus atoms (2.16):



This gives rise to a net reaction for conversion of (2.14) to S, S, S-trialkyltetraphosphate, dialkylsulfide, and S-alkylthiophosphate di-anion as shown in (2.17):



The dialkylsulfide and S,S,S-trialkyltetraphosphate decomposition products are soluble in oil.

The S-alkylthiophosphate decomposition product can also react with itself by way of a phosphoryl nucleophilic attack and elimination of mercaptide anion as in reaction (2.15). This process will continue until a zinc pyro- and polypyrophosphate molecule with low sulfur content is formed. The chain will continue to extend until the product precipitates out of solution.

The decomposition of primary alkyl ZDDPs can be accurately described as above. Zinc dialkylldithiophosphates made from branched primary alcohols will decompose in a similar fashion, although at a much slower rate. This can be explained by the fact that the alpha carbon of the branched primary alkyl group, being more sterically hindered than the unbranched primary alkyl group, will be less

susceptible to nucleophilic attack, as described by reaction (2.9). The increased steric hindrance derived from beta carbon branching will also decrease the amount of successful mercaptide anion attack on the branched alkyl P–O–R bond, resulting in less dialkylsulfide formation and a higher yield of mercaptan and olefin byproducts (through a competing protonation and/or elimination reaction with mercaptide anion). Lengthening the alkyl chain will have a much less pronounced effect on thermal stability than branching at the beta carbon due to the greater steric hindrance derived from the latter.

The decomposition of secondary alkyl ZDDPs, although similar to primary decomposition, shows that olefin formation is much more pronounced. The increase in elimination over nucleophilic substitution in secondary ZDDPs over primary ZDDPs is easily explained by the fact that elimination is accelerated by increasing the alkyl substitution around the forming double bond. Thus, secondary alkyl groups will favor a thermal decomposition into olefins and phosphate acids at the expense of the sulfur-oxygen interchange noted above. In a similar but much more pronounced way, tertiary ZDDP decomposition will be dominated by facile production of olefin through elimination. This occurs at even moderate temperatures, making their use in commercial applications prohibitive.

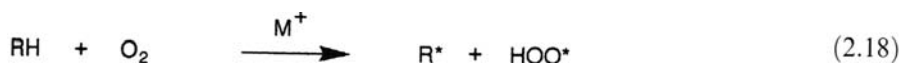
Aryl zinc dialkyldithiophosphates, due to the stability of the aromatic ring, are not susceptible to nucleophilic attack. Thus, the initial thermal decomposition reaction described in reaction (2.9) cannot occur. The formation of olefin from an acid-catalyzed elimination reaction also cannot occur. Aryl ZDDPs are, therefore, very thermally stable.

A rating of the various zinc dialkyldithiophosphates in terms of thermal stability would, therefore, be aryl > branched primary alkyl > primary alkyl > secondary > tertiary. The varying amounts of decomposition products that depend on the heat history and the alkyl or aryl chain involved will directly control the amount of extreme pressure and wear protection the ZDDP will provide in a given circumstance [10].

Hydrolysis of a zinc dialkyldithiophosphate begins with cleavage of the carbon-oxygen bond of the thiophosphate ester, with the hydroxide anion displacing the thiophosphate anion leaving group. The stability of the intermediate alkyl cation determines the ease with which this cleavage takes place. The secondary alkyl cation is more stable and more easily formed than the primary alkyl cation; therefore, hydrolysis of secondary ZDDP occurs more easily than hydrolysis of primary ZDDP. For the case of an aryl ZDDP, the carbon-oxygen bond cannot be broken, and the site of hydrolytic attack is the phosphorus-oxygen bond with displacement of phenoxide anion with hydroxide anion. The order of hydrolytic stability is, therefore, primary > secondary > aryl.

5 OXIDATION INHIBITION

Base oils used in lubricants degrade by an autocatalytic reaction known as *auto-oxidation*. The initial stages of oxidation are characterized by a slow, metal-catalyzed reaction with oxygen to form an alkyl-free radical and a hydroperoxy-free radical as seen in (2.18):



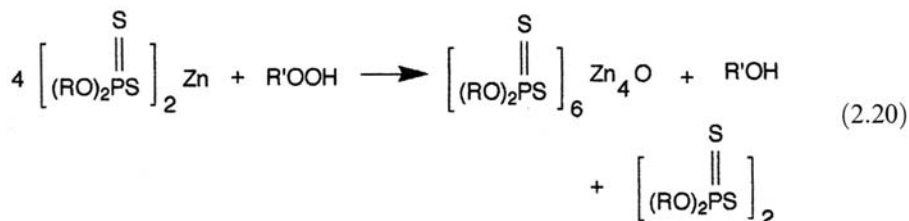
This reaction is propagated by the reaction of the alkyl-free radical with oxygen to form an alkylperoxy radical. This radical further reacts with the base oil hydrocarbon to form alkyl hydroperoxide and another alkyl radical as seen in (2.19):



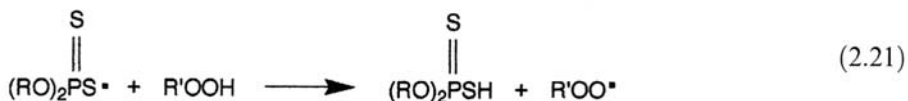
This initial sequence is followed by chain branching and termination reactions forming high-molecular-weight oxidation products [11].

The antioxidant functionality of zinc dialkyldithiophosphate is ascribed to its affinity for peroxy radicals and hydroperoxides in a complex pattern of interaction.

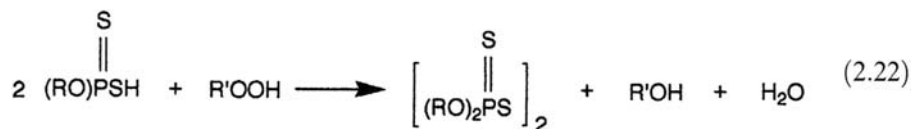
The initial oxidation step of ZDDP by hydroperoxide is the rapid reaction involving the oxidative formation of the basic ZDDP salt as seen in (2.20):



In this reaction, one mole of alkyl hydroperoxide converts four moles of neutral ZDDP to one mole of basic ZDDP and two moles of the dialkyldithiophosphoryl radical (which subsequently reacts to produce the disulfide) [12]. The rate of hydroperoxide decomposition slows during an induction period during which the basic zinc thermally breaks down into the neutral ZDDP and zinc oxide [6]. This is followed by the neutral ZDDP further reacting with hydroperoxide to produce more dialkyldithiophosphoryl disulfide and more basic ZDDP. When the concentration of the basic ZDDP becomes low enough, a final rapid neutral salt-induced decomposition of the hydroperoxide will occur in which the dialkyldithiophosphoryl radical will not react with itself to form the disulfide, but will react with hydroperoxide to form the dialkyldithiophosphoric acid as seen in (2.21) [13]:

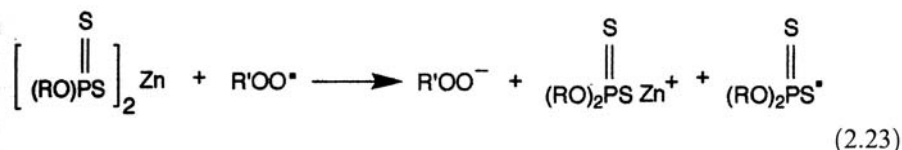


The dialkyldithiophosphoric acid then rapidly reacts with alkyl hydroperoxide, producing oxidation products that are inactive in oxidation chain reactions. The simplest reaction scheme for the reduction of the hydroperoxide is seen in (2.22):



Oxidation products include the disulfide mentioned above, the analogous mono- and trisulfides, and compounds of the form $(RO)_n(RS)_{3-n}P=S$ and $(RO)_n(RS)_{3-n}P=O$ [3]. These products show little activity as either oxidation inhibitors or antiwear agents.

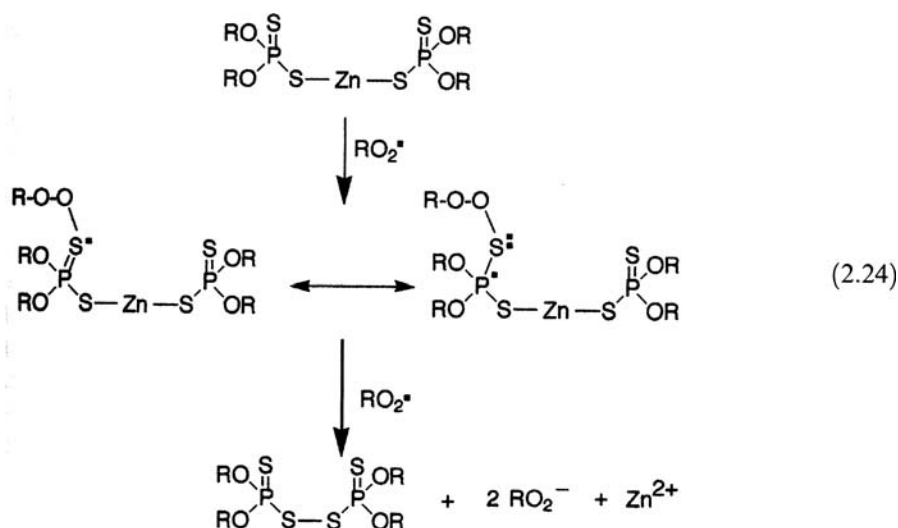
The literature also reveals an ionic process that will produce more dialkyl-dithiophosphoric acid as seen in (2.23):



followed by (2.21) [14].

At low concentrations of ZDDP, hydrolysis of the ZDDP to the zinc basic double salt and dialkyldithiophosphoric acid becomes viable. At temperatures above 125°C, the dialkyldithiophosphoryl disulfide decomposes into the dialkyldithiophosphoryl radicals which further react with hydroperoxide to produce more dialkyl-dithiophosphoric acid [6]. Thus, many pathways are available to form the active dialkyldithiophosphoric acid.

The neutral ZDDP also reacts with alkyl peroxy radicals. This is an electron-transfer mechanism that involves the stabilization of a peroxy intermediate. An attack by a second peroxy radical leads to the intramolecular dimerization of the resulting dithiophosphate radical forming the inactive dialkyldithiophosphoryl disulfide as seen in (2.24):



The zinc metal atom provides an easy route for heterolysis of the radical intermediate, thus the disulfide, by itself, has little antioxidant functionality [15]. Zinc dialkyldithiophosphate acts as an oxidation inhibitor not only by trapping the alkyl radicals, thus slowing the chain reaction mechanism, but also by destroying alkyl hyperperoxides and inhibiting the formation of alkyl radicals. Empirical determination of the relative antioxidant capability of the three main classes of ZDDP shows secondary ZDDP > primary > aryl ZDDP. The relative performance of each ZDDP type may correlate with the stabilization of the dialkyl(aryl)dithiophosphoryl radical and its subsequent reactivity with alkyl hydroperoxide to produce the catalyzing acid.

Commercial ZDDPs are a mixture of both neutral and basic salts. It has recently been determined that neutral and basic ZDDPs give essentially equivalent performance with respect to antioxidant behavior. This can be explained by the equilibrium shown in (2.8). At elevated temperatures, as would occur in an oxidation test, the basic ZDDP is converted into the neutral ZDDP. As the temperature is lowered, the equilibrium shifts back toward the formation of the basic ZDDP, indicating that the concentration of basic ZDDP is a function of temperature. The solvent used and the presence of other additives also play a role in this equilibrium. Thus, the exact composition of neutral versus basic salts at any time in an actual formulation is a complex function of many variables.

6 ANTIWEAR AND EXTREME-PRESSURE FILM FORMATION

Zinc dialkyldithiophosphates operate mainly as antiwear agents but exhibit mild extreme-pressure characteristics. As an antiwear agent, ZDDP operates under mixed lubrication conditions with a thin oil film separating the metal parts. Surface asperities, however, intermittently penetrate the liquid film, giving rise to metal-on-metal contact. The ZDDP reacts with these asperities to reduce this contact. Likewise, when the load is high enough that the oil film collapses, the ZDDP reacts with the entire metal surface to prevent welding and reduce wear. A great deal of study has been done to determine the nature of this protective film and the mechanism of deposition, where the thermal degradation products of the ZDDP are the active antiwear agents.

The antiwear film thickness and composition are directly related to temperature and the extent of surface rubbing. Initially, ZDDP is reversibly absorbed onto the metal surface at low temperatures. As the temperature increases, catalytic decomposition of ZDDP to dialkyldithiophosphoryl disulfide occurs, with the disulfide absorbed onto the metal surface. From here, the thermal degradation products (as described in Section 3) are formed with increasing temperature and pressure until a film is formed on the surface [16]. The thickness and composition of this film have been studied using many different analytical techniques, but no one analysis gives a concise description of the film size and composition for the various kinds of metal-to-metal contact found in industrial and automotive lubrication regimes. In general, the antiwear/extreme-pressure ZDDP film can be said to be composed of various layers of ZDDP degradation products. Some of these degradation products are reacted with the metal making up the lubricated surface. The composition of the layers is temperature-dependent.

The first process that takes place is the reaction of sulfur (from the ZDDP thermal degradation products) with the exposed metal leading to the formation of a thin iron sulfide layer [17]. Next, phosphate reacts to produce an amorphous layer of short-chain ortho- and metaphosphates with minor sulfur incorporation. The phosphate chains become longer toward the surface, with the minimum chain length approaching 20 phosphate units. Some studies have indicated that this region is best described as a phosphate “glass” region in which zinc and iron cations act to stabilize the “glass” structure. At the outermost region of the antiwear film, the phosphate chains contain more and more organic ligands, eventually giving way to a region comprised of organic ZDDP decomposition products and undegraded ZDDP itself. The thickness of the film has been analyzed to be as small as 20 nanometers

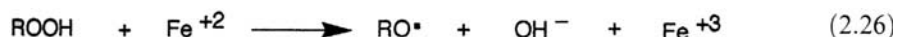
using ultrathin film interferometry and as large as 1 micron using electrical capacitance [18–21].

Recent work has concluded that, although the rate of the film formation is directly proportional to temperature, a stronger correlation exists between film formation and the extent of metal-to-metal rubbing as quantified by the actual distance that the metal slides during a given test period. The film reaches a maximum thickness at which point a steady state between formation and removal exists, the rate of formation being more temperature-dependent than the rate of removal. It was also found that the ZDDP reaction film has a “solidlike” nature (as opposed to being a highly viscous liquid) due to the lack of a reduction of film thickness observed with time on a static test ball [22].

Another mechanism of wear found to be inhibited by zinc dialkyldithiophosphate is wear produced from the reaction of alkyl hydroperoxides with metal surfaces. It was found that the wear rate of automobile engines cam lobes is directly proportional to alkyl hydroperoxide concentration. The mechanism proposes the direct attack of hydroperoxide (generated via fuel combustion and oil oxidation) on fresh metal, causing the oxidation of an iron atom from a neutral charge state to Fe^{+3} by reaction with three moles of alkyl hydroperoxide as described by reactions (2.25):



and (2.26):



The ZDDP and its thermal degradation products neutralize the effect of the hydroperoxides by the mechanism described in reactions (2.20)–(2.23) in Section 5. It was also shown that peroxy and alkoxy radicals were far less aggressive toward metal surfaces than hydroperoxides, indicating that free-radical scavengers, such as hindered phenols, would be ineffective in controlling this kind of engine wear. This may explain why the antiwear performance of ZDDP is directly related to its anti-oxidation performance in the order of secondary ZDDP > primary ZDDP > aryl ZDDP rather than correlating with the order of thermal stability (aryl > primary > secondary) [23].

A recent study has been conducted to investigate the difference in wear performance between neutral and basic ZDDPs in the Sequence VE engine test. The neutral ZDDP performed better in value train wear protection than the basic ZDDP. The basic salt actually failed the Sequence VE engine test, indicating that using commercial ZDDPs with lower basic salt content may be preferred when limited to a 0.1% maximum phosphorus content (as mandated by the I.L.S.A.C. GF-3 motor oil specification). It was suggested that the increased wear protection by neutral ZDDP could be explained by the superior adsorption of the oligomeric structure of the neutral salt, leading to the formation of longer polyphosphate chains relative to the basic salt [5].

7 APPLICATIONS

Zinc dialkyldithiophosphates are used in engine oils as antiwear and antioxidant agents. Primary and secondary ZDDPs are both used in engine oil formulations,

but it has been determined that secondary ZDDPs perform better in cam lobe wear protection than primary ZDDPs. Secondary ZDDPs are generally used when increased extreme-pressure activity is required (i.e., during run-in to protect heavily loaded contacts such as valve trains). Zinc dialkyldithiophosphates are generally used in combination with detergents and dispersants (alkaline earth sulfonate or phenate salts, polyalkenyl succinic amides or Mannich-type dispersants), viscosity index improvers, additional organic antioxidants (hindered phenols, alkyl diphenyl amines), and pour point depressants. A typical lubricant additive package for engine oils can run as high as 25% in treatment level. The International Lubricant Standardization and Approval Committee (ILSAC) has designated its GF-3 engine oil specification to include a maximum limit of 0.1% phosphorus to minimize the engine oil's negative impact on the emissions catalyst. For the GF-4 specification, scheduled to take effect in 2004, the limit may be reduced even further if an acceptable Oil Protection of Emission Systems Test (OPEST II), which would replace the minimum phosphorus requirement, cannot be developed. As a result of this minimum phosphorus requirement, the treatment level for zinc dialkyldithiophosphate in engine oil is limited to about 0.5–1.5%, depending on the alkyl chain length used.

The new challenge to motor oil formulators is in passing the required ILSAC tests while keeping the ZDDP level low. Yamaguchi et al. have shown that the antioxidant effect of ZDDP is significantly enhanced in API group II base stocks with as much as a 50% increase noted for a basic ZDDP. An increase in antioxidancy was also noted when using ZDDPs in polyol ester [24]. Several studies have also shown that ZDDP oxidation byproducts are ineffective antiwear agents. The use of these base stock effects to extend the oxidation life of the ZDDP may be a suitable method for the formulator to reduce the level of ZDDP needed to accommodate the GF-3 limits.

The synergistic effect between organic molybdenum compounds and ZDDP in wear reduction is currently being studied as a means of lowering phosphorus content in engine oils. In U.S. patent 5,736,491, a molybdenum carboxylate is used with a ZDDP to give a synergistic reduction in friction coefficient by as much as 30%, thus allowing a reduction in total phosphorus content and improved fuel economy [25]. The patent literature has cited other organic molybdenum compounds such as molybdenum dithiocarbamates (MoDTC) and dialkyldithiophosphates (MoDTP) as being useful, synergistic secondary antiwear agents.

Zinc dialkyldithiophosphates are also used in hydraulic fluids as antiwear and antioxidants. The treatment level for ZDDP in hydraulic fluids is lower than that used for engine oils, typically running between 0.2–0.7% by weight. They are used in combination with detergents, dispersants, additional organic antioxidants, viscosity index improvers, pour point depressants, corrosion inhibitors, defoamers, and demulsifiers for a total treatment level of between 0.5 and 1.25% [27]. Primary ZDDPs are preferred over secondary ZDDPs due to their better thermal and hydrolytic stability. One problem facing hydraulic fluid formulators is the need for a fluid that will service both high-pressure rotary vane pumps and axial piston pumps, preferably out of the same sump. High-pressure vane pumps require a hydraulic fluid with antiwear properties and oxidative stability commonly achieved through the use of zinc dialkyldithiophosphates. High-pressure piston pumps need only rust and oxidation protection and do not require ZDDPs. Zinc dialkyldithiophosphates can cause catastrophic failure to axial piston pump systems by adversely affecting the

sliding steel-copper alloy interfaces. The patent literature has several examples of formulators trying to overcome this problem with the use of additional wear-moderating chemistries such as sulfurized olefins, polyol esters or borates of them, fatty acid imidazolines, aliphatic amines, and polyamines. Another problem facing hydraulic fluid formulators is the interaction of ZDDPs with overbased alkaline earth detergent salts (as well as the interaction of carboxylic acid and alkenyl succinic anhydride rust preventatives with these detergents) in the presence of water to give filter-clogging byproducts. Formulators have tried to overcome this problem of poor "wet" filterability by using nonreactive rust inhibitors (i.e., alkenyl succinimides) and improving the hydrolytic stability of the ZDDP antiwear agent [28].

Zinc dialkyldithiophosphates are used in extreme-pressure (EP) applications like gear oils, greases, and metal-working fluids. Secondary ZDDPs are preferred due to their thermal instability with resulting quick film formation under high loads. In automotive gear oils, ZDDPs are used at 1.5–4% in combination with extreme-pressure agents (such as sulfurized olefins), corrosion inhibitors, foam inhibitors, demulsifiers, and detergents. Total multifunctional additive package treatment levels for automotive gear lubricant additives are from 5–12% by weight. Industrial gear oil formulators have generally gone to ashless systems using sulfur-phosphorus-based extreme-pressure antiwear chemistries at total additive package treatment levels of 1.5–3%. In general, the recent focus in gear oil technology improvement has centered on increased thermal stability and extreme-pressure properties.

Zinc dialkyldithiophosphates are used in greases in chemical systems that closely resemble gear oil formulations. Many gear oil lubricant additives are used in extreme-pressure greases. In general, the ZDDP treatment level for greases is in the same range as that used for gear oils. The ZDDP, usually secondary or a mixture of secondary and primary, is used in combination with sulfurized olefins, corrosion inhibitors, ashless antioxidants, and additional friction modifiers. A recent advancement in grease technology is the use of ZDDP/sulfurized olefin synergy to replace antimony and lead in high-EP grease formulations. This has generally been limited to the European market, having been pioneered in Germany.

Zinc dialkyldithiophosphates, in combination with sulfurized olefins, are also used to replace chlorinated paraffins in medium- to heavy-duty metal-working fluids. This is due to the possible carcinogenicity of the low-molecular-weight analogs of chlorinated paraffin. European formulators, and to a certain extent Japanese formulators, use ZDDPs in this way. The use of ZDDPs in metal-working fluids in the United States is limited due to environmental concerns. The U.S. Environmental Protection Agency classifies them as marine pollutants.

In conclusion, after 50 years, zinc dialkyldithiophosphates still enjoy a wide variety of uses in the lubrication industry, with production volumes remaining at high levels. The majority of ZDDP production is used in automobile engine oil. The impact of the GF-2 and GF-3 phosphorus level specification of 0.1%, however, has been to reduce ZDDP production in the last 10 years. The Ford Motor Company is currently evaluating engine oils with 0–0.6% phosphorus levels in fleet tests in preparation for the looming GF-4 standard in 2004, which will require engine oils to have minimal impact on emission system deterioration. This could further negatively impact ZDDP production. The need to understand clearly how ZDDPs function in terms of wear and oxidation protection is reinforced by the need to develop satisfactory phosphorus-free alternatives to ZDDP. The development of such

chemistries, within the economic and functional limits that ZDDPs impose, will be a daunting task for future researchers. Until that time, the elimination of zinc dialkyl-dithiophosphates from various industrial lubricants will mandate either higher costs or less performance.

REFERENCES

1. HC Freuler. Modified lubricating oil. U.S. Patent 2,364,284 (12/5/44, Union Oil Co. of California).
2. DR Adams. Manufacture of dihydrocarbyl dithiophosphates. U.S. Patent 5,672,294 (5/6/97, Exxon Chemical Patents, Inc.).
3. JL Paddy et al. Zinc dialkyldithiophosphate oxidation by cumene hydroperoxide: Kinetic studies by Raman and ^{31}P NMR spectroscopy. *Trib Trans* 33(1): 15–20, 1990.
4. ES Yamaguchi et al. Dynamic light scattering studies of neutral diisobutyl zinc dithiophosphate. *Trib Trans* 40(2):330–337, 1997.
5. ES Yamaguchi. The relative wear performance of neutral and basic zinc dithiophosphates in engines. *Trib Trans* 42(1):90–94, 1999.
6. AJ Bridgewater, JR Dever, MD Sexton. Mechanisms of antioxidant action, part 2. Reactions of zinc bis{O,O'-dialkyl(aryl)phosphorodithioates} and related compounds with hydroperoxides. *J Chem Soc Perkin II*, 1006–1016, 1980.
7. TF Buckley. Methods for preventing the precipitation of mixed zinc dialkyldithiophosphates which contain high percentages of a lower alkyl group. U.S. Patent 4,577,037 (3/18/86, Chevron Research Co.).
8. ES Yamaguchi. Oil soluble metal (lower) dialkyl dithiophosphate succinimide complex and lubricating oil compositions containing same. U.S. Patent 4,306,984 (12/22/81, Chevron Research Co.).
9. H Luther, E Baumgarten, K Ul-Islam. Investigations by gas chromatography into the thermal decomposition of zinc dibutyldithiophosphates. *Erdol und Kohle* 26(9):501, 1973.
10. RC Coy, RB Jones. The chemistry of the thermal degradation of zinc dialkyldithiophosphate additives. *ASLE Trans* 24(1):91–97, 1979.
11. M Rasberger. Oxidative degradation and stabilization of mineral based lubricants, in RM Moritier and ST Orszulik, eds. *Chemistry and Technology of Lubricants*, 2nd ed. London: Blackie Academic and Professional, 1997, pp. 82–123.
12. E Rossi, L Imperato. *Chim Ind (Milan)* 53:838–840, 1971.
13. MD Sexton. *J Chem Soc Perkin Trans II* 1771–1776, 1984.
14. SA Howard, SB Tong. *Can J Chem* 58:92–95, 1980.
15. AJ Burn. The mechanism of the antioxidant action of zinc dialkyl dithiophosphates. *Tetrahedron* 22:2153–2161, 1966.
16. CH Bovington, B Darcre. The adsorption and reaction of decomposition products of zinc dialkyldithiophosphate on steel. *ASLE Trans* 27:252–258, 1984.
17. JC Bell, KM Delargy. The composition and structure of model zinc dialkyldithiophosphate antiwear films. *Proc. 6th Intl Cong on Trib Eurotrib '93*, Budapest, M Kozna, ed., 2:328–332, 1993.
18. PA Willermet, RO Carter, EN Boulos. Lubricant-derived tribochemical films—An infra-red spectroscopic study. *Trib Intl* 25:371–380, 1992.
19. M Fuller et al. Chemical characterization of tribochemical and thermal films generated from neutral and basic ZDDPs using x-ray absorption spectroscopy. *Trib Intl* 30:305–315, 1997.
20. AF Alliston-Greiner, JA Greenwood, A Cameron. Thickness measurements and mechanical properties of reaction films formed by zinc dialkyldithiophosphate during

- running. Proc IMechE Intl Conf Tribology—Friction, lubrication and wear 50 years on, London, IMechE. 1:565–569, 1987.
21. G Tripaldi, A Vettor, HA Spikes. Friction behavior of ZDDP films in the mixed boundary/EHD regime. SAE Tech. paper 962036, 1996.
 22. L Taylor, A Dratva, HA Spikes. Friction and wear behavior of zinc dialkyldithiophosphate additive 43(3):469–479, 2000.
 23. JJ Habeeb, WH Stover. The role of hydroperoxides in engine wear and the effect of zinc dialkyldithiophosphates. A.S.L.E. Trans 30(4):419–426, 1987.
 24. ES Yamaguchi et al. The relative oxidation inhibition performance of some neutral and basic zinc dithiophosphate salts. S.T.L.E. Preprint No. 99-AM-24, pp. 1–7, 1999.
 25. JA Patel. Method of improving the fuel economy characteristics of a lubricant by friction reduction and compositions useful therein. U.S. Patent 5,736,491 (4/7/98, Texaco, Inc.).
 26. Y Naitoh. Engine oil composition. U.S. Patent 6,063,741 (5/16/2000, Japan Energy Corporation).
 27. SH Brown. Hydraulic system using an improved antiwear hydraulic fluid. U.S. Patent 5,849,675 (12/15/98, Chevron Chemical Co.).
 28. HT Ryan. Hydraulic fluids. U.S. Patent 5,767,045 (6/16/98, Ethyl Petroleum Additives, Ltd.).

Ashless Phosphorus-Containing Lubricating Oil Additives

W. DAVID PHILLIPS

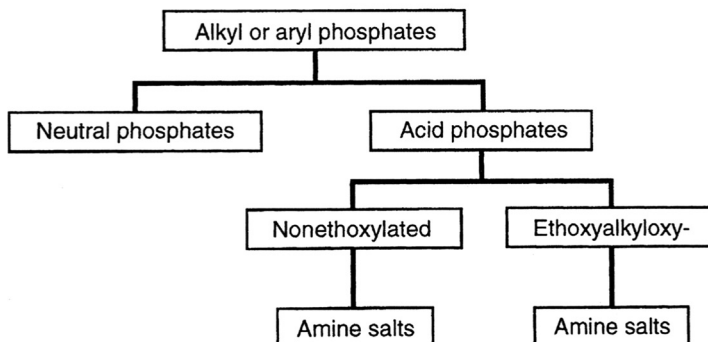
*Performance Additives and Fluids Business, Great Lakes Chemical Corp.,
Manchester, England*

1 INTRODUCTION AND SCOPE

In any discussion of phosphorus-containing lubricating oil additives, the products that probably come most rapidly to mind are the zinc dialkyldithiophosphates—multifunctional additives that have been widely used in both automotive and industrial oils for many years. However, a wide variety of ashless phosphorus-containing additives is used in the lubricating oil industry. As with the metal-containing dithiophosphates, they have been in use over a long period and, despite considerable research into alternative chemistries, the basic structures introduced in the 1930s are still in use today. In contrast, the technology of most other additive types and that of the base stocks themselves have steadily developed over this time. Many different types of phosphorus-containing molecules have been examined as additives for lubricating oils, with most attention given to their potential as antiwear and extreme-pressure additives. Consequently, the patent literature contains a host of references to different structures displaying this characteristic. However, regardless of structure, all the additives used in this application serve the same and specific function of bringing phosphorus into contact with the metal surface, where it can be adsorbed and, under certain conditions, react. The resulting surface film improves the lubrication properties of both mineral and synthetic oils.

This chapter discusses the use of chemicals that contain only phosphorus to improve the performance characteristics of oils, specifically neutral and acid phosphates, phosphites and phosphonates, and the amine salts of the acids (see [Figures 1](#) and [2](#) for an outline of the main classes and their structures). These are

1 Phosphate esters



2 Phosphites and phosphonates

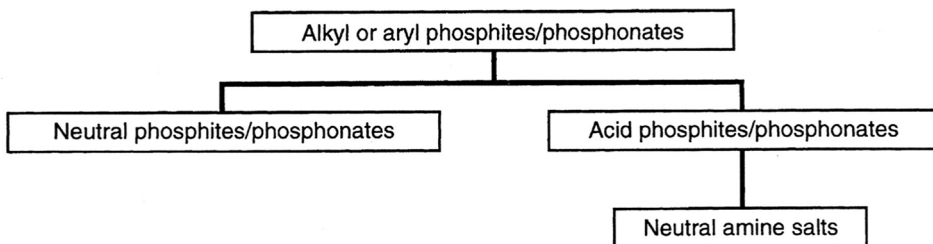


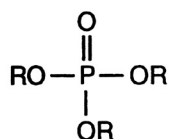
Figure 1 Main classes of phosphorous-containing additives for lubricating oils.

the principal types of phosphorus compounds in current commercial use, but other types have also been examined and claimed in the patent literature, for example, phosphoramidates. There are also ashless compounds where sulfur or chlorine has been incorporated into the molecule as, for example, in thiophosphates and chlorinated phosphates. These are outside the scope of this discussion, but the performance of combinations of compounds separately containing phosphorus and sulfur or chlorine will be mentioned.

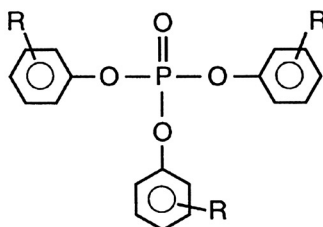
In addition to examining the impact of ashless phosphorus compounds on lubrication performance, this chapter also looks at their performance as antioxidants, rust inhibitors, and metal passivators. Their polar nature also makes them good solvents and assists the solution of other additives in nonpolar base stocks. The versatility displayed by phosphorus-containing additives is such that usage of these products continues to grow nearly half a century after their introduction, and they find application in the latest technological developments.

2 HISTORICAL BACKGROUND

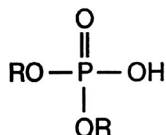
Until the 1920s, additive-free mineral oils met the majority of industry's lubrication requirements. In the applications where their performance was unsatisfactory, an increase in viscosity and/or the sulfur content of the oils then available usually provided adequate lubrication. For very severe applications, the oil would be blended



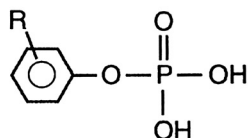
Trialkyl phosphate



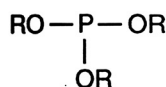
Triaryl phosphate



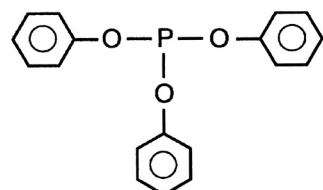
Alkyl monoacid phosphate



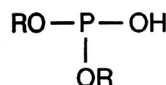
Aryl diacid phosphate



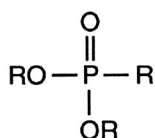
Trialkyl phosphite



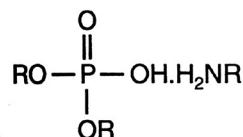
Triaryl phosphite



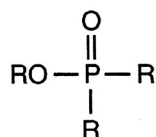
Dialkyl phosphite



Dialkyl alkyl phosphonate



Amine phosphate



Alkyl dialkyl phosphinate

Figure 2 The structures of some common phosphorous-containing lubricating oil additives.

with animal or vegetable oils; for example, tallow or rapeseed oils were used for steam engine cylinder lubrication. Fish oils were used in the early locomotive axle boxes, castor oil reduced friction in worm gear drives, and flowers of sulphur were added to cutting oils. However, when hypoid gears were introduced, they quickly revealed the limited lubrication of the oils then available. This resulted in the development of additives such as sulfurized lard oil and lead naphthenate. These were followed

by sulfurized sperm oil, an additive that eventually became widely used in both industrial and automotive applications.

The earliest type of organic phosphorus chemical to find use as a lubricating oil additive is thought to have been a neutral triaryl phosphate, specifically tricresyl phosphate (TCP). This material was originally synthesized about 1854 [1] although trialkyl phosphates were synthesized slightly earlier, in about 1849 [2]. Commercial production of TCP began about 1919, when this product was introduced as a plasticizer for cellulose nitrate, but it was not until the 1930s that patents began to appear claiming improved lubrication when TCP was blended into mineral oil. In 1936 this use was claimed in gear oils [3], but a detailed investigation into their behavior as antiwear (AW) additives was not published until 1940 [4,5], by which time TCP was already said to be in widespread use. During World War II, extensive research took place in Germany into phosphorus-containing additives [6,7]. This research was facilitated by the recent availability of test equipment for assessing wear and load-carrying behavior, for example the four-ball machine [8]. The results of the research concluded that, for high load-carrying (later known as extreme-pressure, or EP) performance, the molecule must contain

A phosphorus atom

Another active group, e.g. Cl^- or OH^- (for attachment to the metal surface)

At least one aryl or alkyl group (phosphoric acid was not thought to be active)

Subsequent to these studies the market adopted chlorine-containing phosphates, such as tris-(2-chloroethyl) phosphate, but they were later replaced in most applications by other EP additives as the chlorine tended to produce corrosion.

The 1940s and 1950s saw significant development activity in the oil industry involving TCP, and patents appeared claiming the use of this AW/EP additive in general industrial oils [9], rolling oils [10], cutting oils [11], greases [12], rock drill lubricants [13], and aviation gas turbine lubricants [14,15]. Some military specifications, for example on hydraulic oils (NATO codes H515/520/576), were published which initially called for the use of this additive. However, in the late 1960s the difficulty of obtaining good-quality feedstocks for the manufacture of "natural" phosphates based on cresol and xylene, together with the concern regarding the neurotoxicity of TCP [16,17], led to the reformulation of many products with the less toxic synthetic triaryl phosphates. TCP is still used today in some applications, but the quality of the phosphate in terms of its purity and freedom from the ortho-cresol isomer, which was mainly responsible for the neurotoxicity behavior, has improved substantially in the last 10 to 15 years.

In addition to its use as an oil additive, TCP was also used for a period in the 1960s as an ignition control additive for motor gasoline in order to avoid pre-ignition arising from the deposition of lead salts. These were formed by the interaction of the lead tetraethyl antiknock additive and the alkyl halide scavenger [18–21]. Alkyl phosphates were claimed for this application in 1970 [22].

As a result of their polar nature, neutral triaryl phosphates have also been claimed as corrosion inhibitors for hydrocarbons [23,24], but they are unlikely to be promoted for this application today in view of the availability of more active species, such as the acid phosphates.

The use of trialkyl phosphates as antiwear and extreme-pressure additives has been much less extensively evaluated. While a flurry of patent activity took place in

the late 1920s and 1930s covering methods of their manufacture [25–34], there was little interest in their use as lubricating oil additives for a further 20 years. This was probably a result of the focus, in the interim period, on chlorinated derivatives. It was not until the late 1950s that tributyl phosphate (TBP) was disclosed in blends with isopropyl oleate [35] for use in gear oils and claimed in blends with chlorinated aromatics. In 1967 a patent appeared claiming the use of alkyl phosphates or the amine salts of alkyl acid phosphates in water-based lubricating compositions [36].

In addition to alkyl phosphates, various other types of phosphorus-containing compounds have been evaluated as AW/EP additives. Patents on acid phosphates claiming their use as EP additives for oil appeared in 1935 and 1936 [37–39], while the first publication with detailed information on the use of ethoxylated alkyl or aryl phosphates oil additives (in metal-working applications) appeared in 1964 [40]. Patents appeared later on the use of these products in mineral oils [41] and in synthetic esters [42]. Alkoxyated acid phosphates were also found to have good rust inhibition properties [43], a feature that was additionally observed for the alkyl (or aryl) acid phosphates [44,45].

Neutral amine salts of alkyl acid phosphates were claimed in 1964 [46] and, in 1969, in admixture with neutral phosphates [47]. These are, however, just a few examples of the patent estate covering these product groups.

The other main phosphorus-containing products to be discussed are the phosphites. The basic chemistry of alkyl and aryl phosphites, like that of the phosphate esters, was also uncovered in the 19th century. In a similar fashion, their utilization as oil additives was not exploited until much later. Patents appeared in 1940 on the use of mixed aryl phosphites as oil antioxidants [48] and on their acitivity as AW/EP additives at least as early as 1943 [49].

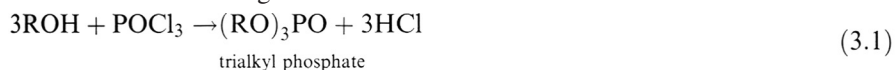
Isomeric with the acid phosphites are phosphonates (Figure 2). Dialkyl alkyl phosphonates were claimed as lubricants in 1952 and 1953 [50,51] but not until about 1971 as friction modifiers and EP additives [52,53].

The above summary has focused on the use of phosphorus compounds alone. In reality they are widely used in admixtures with sulfur-containing materials to provide good lubrication over a wider range of performance requirements. Examples of some of the combinations patented are given in Appendix 2.

3 MANUFACTURE OF PHOSPHORUS-CONTAINING LUBRICATING OIL ADDITIVES

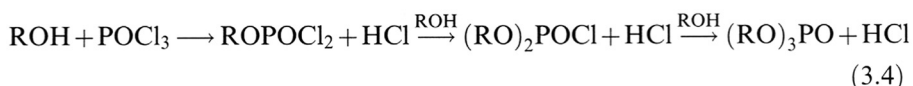
3.1 Neutral Alkyl and Aryl Phosphate Esters

Although phosphate esters can be regarded as “salts” of orthophosphoric acid, they are not currently produced from this raw material because the yields are relatively low (~70% for triaryl phosphates). Instead phosphorus oxychloride (POCl_3) is reacted with either an alcohol (ROH), a phenol (ArOH), or an alkoxide (RONa) as indicated in the following reaction schemes:





The above reactions pass through intermediate steps in the production as shown in scheme (4):



The intermediate products are called *phosphorochloridates*, and, if desired, it is possible to obtain a mixture rich in a particular intermediate by changing the ratio of reactants. The production of mixed products can be achieved by using different alcohols or by an alcohol and an alkoxide (5). These materials are not in significant use as AW/EP additives.



Trialkyl (or alkoxyalkyl) phosphates can be produced by either route (3.1) or (3.3), although in reaction (3.1), unless catalyzed, a considerably excess of alcohol is required to drive the reaction to completion. The hydrogen chloride (HCl) byproduct is removed as rapidly as possible—usually by vacuum and/or water washing while the reaction temperature is controlled in order to minimize the thermal degradation of the phosphate. In the alkoxide route (3.3), the chlorine precipitates as sodium chloride (NaCl), somewhat simplifying the purification treatment. After a water wash to remove the NaCl, purification consists of a distillation step to remove excess alcohol, an alkaline wash, and a final distillation to remove water [54]. With the alkoxide method, any residual chloride can be removed by water washing followed by a final distillation under vacuum.

Despite early research into the alkyl phosphates a rigorous investigation into the preparation of the lower alkyl derivatives and their properties did not take place until 1930 [55]. In contrast to the large range of aryl phosphates available, the range of neutral alkyl phosphates is currently limited to tri-*n*-butyl- and tri-*iso*-butyl phosphate, trioctyl phosphate, and tributoxyethyl phosphate. Other ether phosphates [56] have been claimed in the past but, as far as is known, are not currently manufactured.

Although the neutral trialkyl phosphates have been available for some time, they have not been widely used as additives for mineral oil. Those products in commercial production are used principally as components of aircraft hydraulic fluids or as solvents in industrial processes. However, interest in these materials as antiwear additives for applications where the release of phenols from the degradation of the phosphate is to be avoided, currently exists. They also offer advantages as alternatives to the acid phosphates, alkoxylated acid phosphates, and their salts in metal-working applications, where there are concerns over instability in hard water and foam production in use [57].

Triaryl phosphates, which are the most widely used of all ashless phosphorus-based antiwear additives, are manufactured almost exclusively by reaction (3.2). Phosphorus oxychloride is added to the reaction mass containing an excess of phenol in the presence of a small amount of catalyst, typically aluminum chloride or magnesium chloride, before heating slowly. The hydrogen chloride is removed as it is

formed by heating under vacuum, followed by absorption in water. On completion of the reaction the product is distilled to remove most of the excess phenol(s), the catalyst residue, and traces of polyphosphates. Finally, the product may be steam-stripped to remove volatiles including residual phenol(s) and dried under vacuum.

The raw material for the manufacture of triaryl phosphates was originally obtained from the destructive distillation of coal. This process yields coal tar, which is a complex mixture of phenol and alkyl phenols including cresols and xylenols. Distillation of this mixture (sometimes known as cresylic acids) produces feedstocks rich in cresols and xylenols that are then converted into the neutral phosphate. An early patent on the production of triaryl phosphates from tar acids was issued in 1932 [58].

Unfortunately, in the 1960s, as the number of coal tar distillers declined due to the move from coal to natural gas as a fuel, it became progressively more difficult to obtain cresols and xylenols from this source. As a consequence, the phosphate manufacturers turned their attention to the use of phenol, which was alkylated with propylene or butylene. The resultant mixtures of alkylated phenols were then converted into phosphates [59,60]. To distinguish phosphates from these two sources of raw materials, the cresol- and xylene-based products became known as “natural” phosphates and the phosphates from alkylated phenols as “synthetic” phosphates. This distinction is no longer correct today as synthetic cresols and xylenols are now available and used in phosphate manufacture. The nomenclature, however, remains a simple way of distinguishing between the cresol/xylene-based products and the newer products based on phenol. As the physical and chemical properties of each product type are slightly different, customer selection may depend on the application. For example, if the requirement is for a product that requires good oxidation stability, then the choice would be a tertiarybutylphenyl phosphate, but a xylyl phosphate would be selected if the product required the best hydrolytic stability.

3.2 “Natural” Phosphates

The main products available in this category are tricresyl phosphate (TCP) and trixylyl phosphate (TXP) (Figure 3). These products, based on cresols and xylenols, are complex mixtures of isomeric materials [61]. However, the variation in phosphate-isomer distribution, which arises from changes to the feedstock composition, has little impact on antiwear properties. Of greater importance are the actual phosphorus content and the level of impurities present, particularly those which are acidic.

In the past, the tri-orthocresyl phosphate content was a source of much concern in view of the high neurotoxicity of this material (see later section on [toxicity](#)). However, the feedstock currently used most widely for the production of TCP is predominantly a mixture of meta- and para-cresol, and ortho-cresol levels are extremely low.

3.3 Synthetic Phosphates from Isopropylated Phenols

In this case phenol is alkylated with propylene to produce a mixture of isomers of isopropylated phenol (Figure 4). Depending on the reaction conditions and the degree of alkylation, it is possible to produce a range of isopropylated phenyl phosphates (IPPP) with viscosities varying from ISO VG 22 to VG 100. In seeking an alternative product to TCP (an ISO 32 viscosity-grade fluid) the products with the

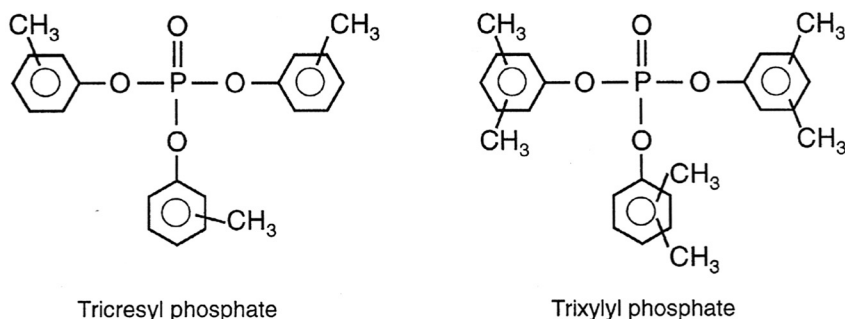


Figure 3 The structures of tricresyl and trixylyl phosphate.

closest phosphorus contents and viscosities (IPPP/22 and IPPP/32) are most widely used.

3.4 Synthetic Phosphates from Tertiarybutylated Phenols

In a similar fashion to the manufacture of isopropylated phenyl phosphates, it is possible to produce a range of phosphates from butylated phenols prepared by the reaction of isobutylene with phenol (Figure 4). The tertiarybutyl substituent is larger in size than the isopropyl substituent, and this reduces the overall level of alkylation in the molecule, resulting in more unsubstituted phenyl groups. Again, the tertiarybutylphenyl phosphates (TBPP) from this range, which are used as antiwear additives in mineral oil, are those closest in phosphorus content and viscosity to TCP, that is TBPP/22 and TBPP/32 (Table 1).

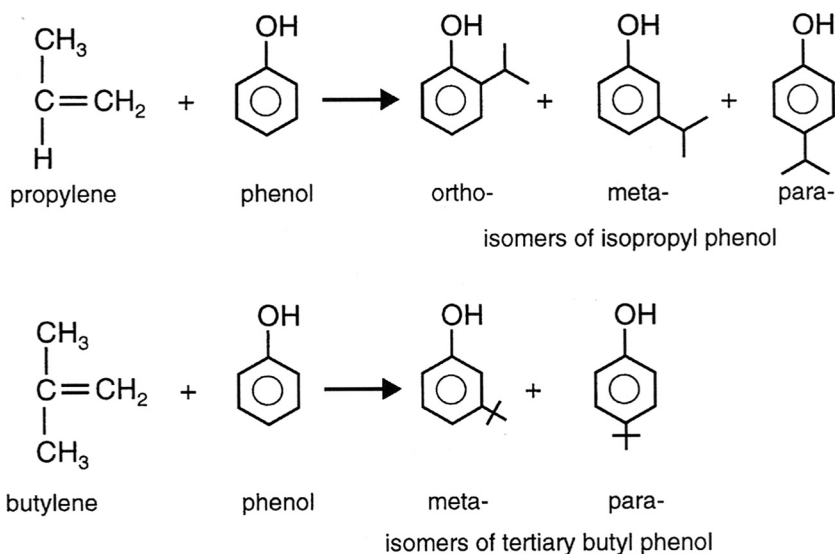


Figure 4 Process for the production of feedstocks used in the manufacture of synthetic phosphates.

Table 1 Phosphorus Contents and Viscosity Levels for Neutral Trialkyl and Triaryl Phosphate Antiwear Additives

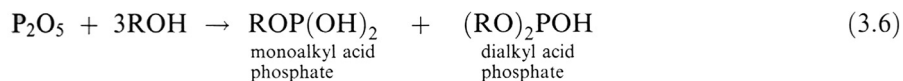
Phosphate ester	Phosphorus content (%)	Typical viscosity at 40°C (cSt)
TiBP	11.7	2.9
TOP	7.8	7.9
TBEP	7.1	6.7
TCP	8.3	25
TXP	7.8	43
IPPP/22	8.3	22
IPPP/32	8.0	32
TBPP/22	8.5	24
TBPP/32	8.1	33
TBPP/100	7.1	95

4 ACID PHOSPHATE ESTERS

4.1 Alkyl and Aryl Acid Phosphates (Nonethoxylated)

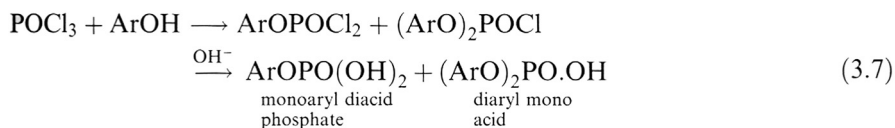
The manufacture of acid phosphates, particularly alkyl acid phosphates, is also based on technology that has its roots in the 19th century but was commercialized only during the last 50 years.

The production process for alkyl acid phosphates is the reaction of phosphorus pentoxide with an alcohol in the absence of water (3.6).



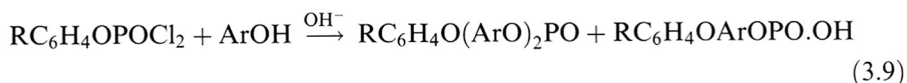
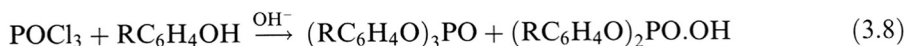
The ratio of monophosphate to diphosphate is usually 40–50% mono- and 50–60% diphosphate, with very small amounts of phosphoric acid ($\leq 1\%$). Some neutral ester may also be produced. Products commercially available are made from C_5 , C_7 , C_8 , and C_9 alcohols, mixtures of C_{10-12} and alcohols, and C_{18} alcohols.

Mono- and diaryl acid phosphates (also known as mono- and diaryl hydrogen phosphates) are byproducts in the manufacture of triaryl phosphates and may be produced by stopping the reaction before completion and hydrolyzing the intermediate phosphorochloridates (3.7).

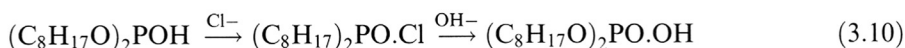


Di(alk)aryl monoacid phosphates, soluble in mineral oil, are reported to be produced by reacting phosphorus oxychloride with an alkylated phenol in the presence of base (3.8) or by the reaction of monoarylphosphorodichloridate with an alkylated phenol (3.9). The reactions are carried out at temperatures of about 60–90°C using lower than equivalent quantities of the phenol. The former process gives predominantly the monoacid phosphate with a small amount of the phosphate ester. The latter produces a somewhat greater amount of the mixed phosphate ester.

but mainly the mixed monoacid phosphate [62]. Examples of commercially available lubricating oil additives of this chemistry are amylphenyl- and octylphenyl acid phosphates.



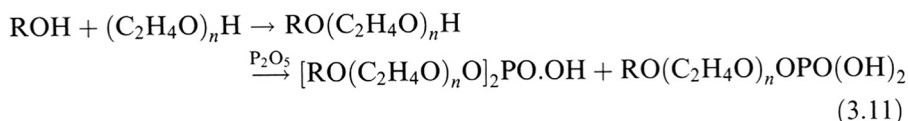
Other processes process reported for the production of mixtures of mono- and di-2-ethylhexyl acid phosphate include the chlorination of bis-(2-ethylhexyl) phosphonate followed by hydrolysis (3.10) or the hydrolysis of tris-(2-ethylhexyl) phosphate.



The alkyl acid phosphates are quite widely used as AW/EP additives in metal-working lubricant applications and as corrosion inhibitors for circulatory oils.

4.2 Alkyl and Alkylaryl/polyethyleneoxy Acid Phosphates

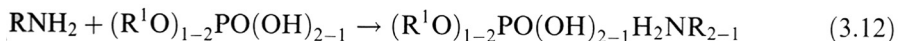
A range of polyethyleneoxy acid phosphate esters was introduced for metal-working lubricant applications in the early 1960s. These products, which consisted of both the free acids and their barium salts, were manufactured by reacting an ethoxylated alcohol with phosphorus pentoxide (3.11). The properties of the resulting acid phosphate mix can vary significantly depending on the chain length of the alcohol and the number of units of ethoxylation. For example, products that are only soluble in oil or water can be produced as well as compounds that are soluble (or dispersible) in both media.



5 AMINE SALTS OF ACID PHOSPHATES AND POLYETHYLENEOXY ACID PHOSPHATES

Although the acidic products are very active AW/EP additives, their acidity can lead to precipitation problems in hard water and potential interaction with other additives. In order to minimize such adverse effects, the acids are sometimes used as their neutral amine (or metal) salt. The salts are produced by reacting an equivalent weight of the base with that of the acid (3.12). The choice of base will vary depending on whether oil or water solubility is required. The use of short-chain amines will normally result in water-soluble additives, while using (say) tertiaryalkyl primary amines with a chain length of C_{11-14} will tend to produce oil-soluble derivatives. The chain length of the acid phosphate also influences the solubility. The selection of the appropriate mixture of amine and phosphate for a given application is largely a compromise because the most active mixtures may also produce disadvantageous side

effects, e.g., on foaming and air release properties. The fact that a neutral salt is used also does not prevent the product from titrating as an acid and from forming a different salt in the presence of the stronger base.



where R is an alkyl group, typically C_8 – C_{22} . It is also possible to use secondary and tertiary amines, R_2NH and R_3N , in the production of these salts.

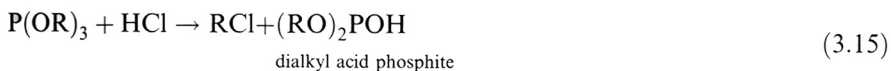
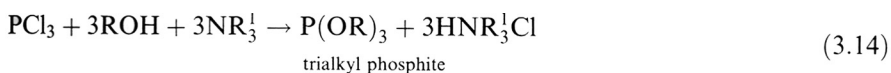
6 NEUTRAL PHOSPHITE ESTERS

As with phosphate esters, it is possible to produce both neutral and acid phosphite esters. The neutral triaryl phosphites are produced by reacting phosphorus trichloride with a phenol or substituted phenol (3.13).

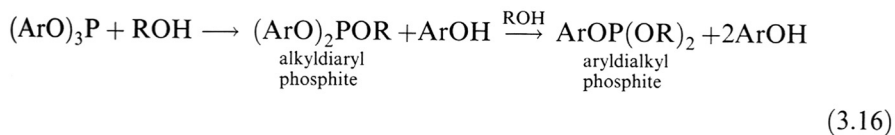


This is also a stepwise process occurring via the production of the di- and mono aryl hydrogen phosphite intermediates.

The production of neutral trialkyl phosphites using PCl_3 requires the addition of a tertiary amine base to neutralize the acid formed (3.14). Unless the HCl is removed quickly, it can cause the process to reverse with the production of an alkyl halide and the dialkyl acid phosphite (3.15).



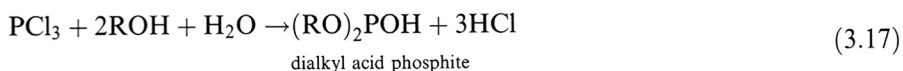
The use of mixtures of different alcohols or different phenols can result in the production of mixed alkyl or aryl phosphites. Mixed alkylaryl phosphites can be produced by reacting triaryl phosphite with alcohols to give a mixture of aryldialkyl and alkyl diaryl phosphites (3.16). A commercial example of such a product promoted as an oil additive is decyldiphenyl phosphite.



Because of their widespread use in the plastics industry as stabilizers for polyvinylchloride, etc., many different neutral phosphites are commercially available. These range from C_2 – C_{18} alkyl (normally saturated) and to C_{1-9} alkaryl. In lubricant applications the most common products are those with alkyl chains of C_8 – C_{18} and C_{8-9} alkaryl, e.g., tris nonylphenyl phosphite and tris-(2,4-ditertiarybutylphenyl) phosphite. The last type is increasingly important in view of its better hydrolytic stability.

7 ALKYL AND ARYL ACID PHOSPHITES

Alkyl and aryl acid phosphites are manufactured by reacting together phosphorus trichloride, an alcohol (or phenol), and water (3.17):

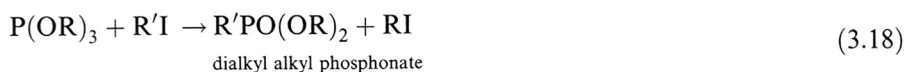


Mixtures of alcohols, as indicated earlier, may also be used to produce di-mixed alkyl phosphites. The commercially available dialkyl acid phosphites vary from C_1 – C_{18} with use as oil additives falling mainly in the range of C_8 – C_{18} .

Little mention is made in the literature of the use of aryl acid phosphites, nor is there any known oil industry use of ethoxylated neutral or acid phosphites. Phosphites are, however, generally unsuitable for applications where water contamination is likely in view of their hydrolytic instability, and ethoxylation, certainly in respect of water-soluble products, would not offer any obvious advantage.

8 DIALKYL ALKYL PHOSPHONATES

Although these products are isomeric with the dialkyl phosphites (Figure 2), they are a distinct class of materials with different properties. They are claimed as friction modifiers as well as AW/EP additives and are prepared by the Arbusov rearrangement in which a trialkyl phosphite is heated with an alkyl halide, e.g., an iodide (3.18):



Commercially available materials range from the dimethyl methyl derivative to products based on dodecyl phosphite, although the higher-molecular-weight products are likely to be of greatest interest for oil applications. Polyethyleneoxy phosphonates, produced by the reaction of diphosphites with epoxides, have been claimed as friction modifiers [63], whereas diaryl hydrogen phosphonates, such as diphenyl phosphonate, are produced by hydrolysis of the corresponding phosphite with water.

9 THE FUNCTION OF LUBRICITY ADDITIVES

The earliest additives used for improving lubrication performance were known as oiliness additives and film strength additives. These descriptions are no longer used and others are now employed. This can lead to some confusion, as the different functions are known by a variety of terms. These are shown in Table 2 together with typical examples of the chemistries employed.

Table 3 [64] offers a generalized classification of the different chemical types of additives used to improve lubrication performance but, depending on the structure of the additive, some variation in the performance can be expected. In reality, the distinction between antiwear and extreme-pressure additives is not clear-cut. Antiwear additives may have mild extreme-pressure properties, while extreme-pressure additives can have moderate antiwear performance, and both produce coatings on the metal surface. In fact, EP additives have been described as additives that reduce or prevent severe wear [65]. However, as seen from the Table 3, EP additives are unlikely to function satisfactorily as friction modifiers, and vice versa.

Table 2 Different Types of Additives Used to Improve Lubrication Performance

Additive type	Purpose	Typical chemistries	Mode of action
Oiliness additive or friction modifier	Reduces friction under near-boundary lubrication conditions	Long-chain fatty acids and esters, sulfurized fatty acids, molybdenum compounds, long-chain phosphites, and phosphonates	Physical adsorption of polar materials on metal surfaces
Antiwear additive (usually with mild EP properties)	Reduces wear at low to medium loads	Neutral organic phosphates and phosphites, zinc thiophosphates	Reacts chemically with the metal surface to form a layer (normally a metal soap) that reduces friction wear at low-medium temperature/loads
Extreme-pressure additive, also known as film strength additive, load-carrying additive, antiseize additive, anticuffing additive	Increases the load at which scuffing, scoring, or seizure occurs	Sulfurized or chlorinated hydrocarbons, acidic phosphorus-containing materials, and mixtures thereof; some metal soaps, e.g. of lead, antimony, and molybdenum	Reacts chemically with the metal surface to form a layer, e.g. as a metal halide or sulfide which reduces friction wear at high temperature/loads.

Table 3 A General Classification of Friction Modifiers, Antiwear and Extreme-Pressure Additives

Additive	Friction modifier	Antiwear additive	Extreme-pressure additive
Natural oils and fats	1	4	5
Long-chain fatty acids, amines, and alcohols	1	4	5
Organo-molybdenum compounds	1	2	4
Synthetic esters	2	3	4
Organo-sulfur compounds	2	2	3
ZDTP	3	1	3
Phosphorus compounds	3	1	3
Sulfur compounds	4	3	1
Chlorine compounds	5	4	1

Source: Ref. 64.

Note: The lower the number, the better the rating.

9.1 The Basic Mechanism of Lubrication and Wear and the Influence of Additives

An understanding of the basic mechanism of lubrication is useful in order to appreciate the way in which additives behave and their relative performance. The following is therefore a somewhat simplified explanation of a relatively complex process.

Lubrication can be described as the ability of an oil (or other liquid) to minimize the wear and scuffing of surfaces in relative motion. It is a function of the properties of the lubricant (for example, viscosity), the applied load, the relative movement of the surfaces (e.g., sliding speeds), temperature, surface roughness, and the nature of the surface film (hardness and reactivity, etc.).

All surfaces are rough. Even those that appear smooth to the naked eye, when examined microscopically, consist of a series of peaks and troughs. The simplest situation arises when the lubricating film is thick enough to completely separate the two surfaces so that metal-to-metal contact does not occur (Figure 5). Such a situation could arise at low loads or with highly viscous liquids, and the lubricating characteristics depend on the properties of the lubricant as the load is fully supported by the lubricant. This condition is known as *hydrodynamic* or *full-film lubrication*.

As the load increases, the lubricating film becomes thinner and eventually reaches a condition where the thickness is similar to the combined height of the asperities on the mating surfaces. At this stage metal contact commences, and as the asperities collide, they are thought to weld momentarily (causing friction) before shearing with loss of metal (wear) (Figure 5). The wear particles may then abrade the surface and adversely affect friction, with the resulting damage depending on the hardness of the particle and the surface it contacts. This condition is known as *mixed-film lubrication* as it is a mixture of full-film lubrication and “boundary lubrication” with the trend toward the latter with increasing load.

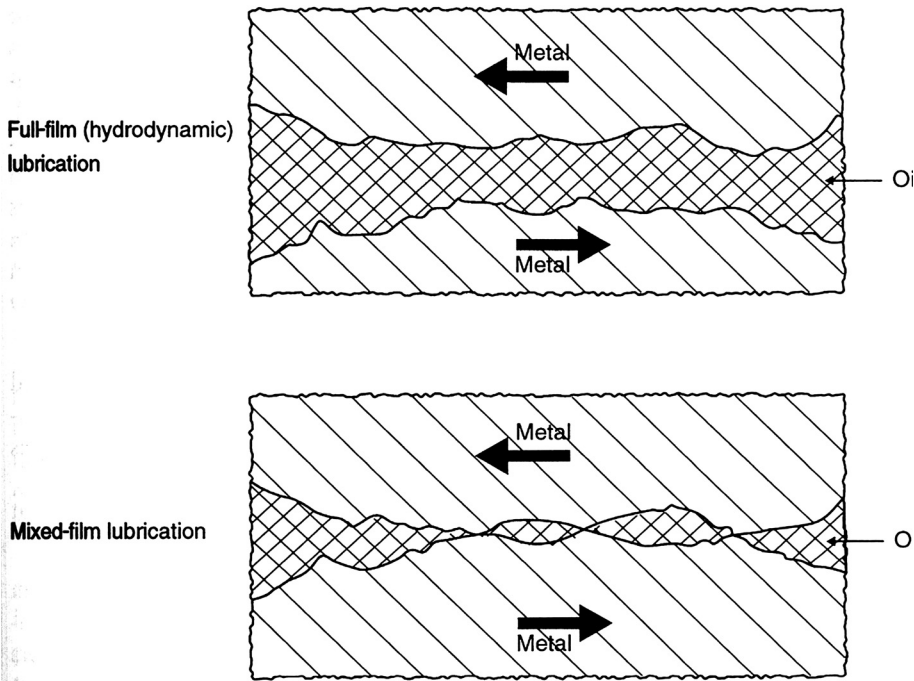


Figure 5 A diagrammatic representation of full-film (hydrodynamic) and mixed-film lubrication.

As the film thins still further, the load is increasingly supported by the metal surface and friction rises rapidly. When eventually a film that is only a few molecules thick separates the surfaces, the roughness, composition, and melting point of the surfaces strongly influence the resulting friction. At this stage viscosity plays little or no part in the frictional behavior. This stage is known as *boundary lubrication* and is characterized by high frictional values that now change little with further increases in load or sliding speed. The wear process that takes place under boundary conditions is perhaps the most complicated of those involved in lubrication in that it involves four different types of wear: corrosive, fatigue, ploughing, and adhesive.

Corrosive wear occurs when the metal surfaces react with their environment to form a boundary film, while fatigue wear is the process of the fracture of asperities from repeated high stress. Micropitting is an example of this form of wear that is the subject of considerable investigation today. Micropitting is the result of plastic deformation of the surface that eventually causes the fracture of the asperity, leaving a small "pit" in the surface. Ploughing wear arises when a sharp particle is forced along the surface, leaving a groove behind, whereas adhesive wear is the tendency of very clean surfaces to adhere to each other. However, this action requires the generation of fresh surfaces during the wear process, perhaps by plastic deformation. It is now thought that this mechanism is much less prevalent than was earlier believed [66].

The relationship between friction and viscosity, load, and sliding speeds can be represented graphically for a bearing by what is known as a *Stribeck curve*. This is shown in Figure 6 [67], where the frictional coefficient is plotted against the dimensionless expression ZN/P . Here Z represents the fluid viscosity, N is the sliding speed, and P is the load. Friction is reduced as the value of ZN/P is lowered until a minimum is reached. For a bearing this minimum value is approximately 0.002 for an ideal hydrodynamic condition. At this point metal contact begins, and friction rises and continues to do so with increasing contact. In the mixed friction zone the friction value lies in the region of 0.02–0.10. Eventually, when the film is very thin, friction becomes independent of viscosity, speed, and load and can reach a value of 0.25. By experiment it was established that

- Continually increasing the load reduced the ZN/P value, assuming speed and viscosity remained constant. The same results can be obtained by reducing either the speed or viscosity, or both, providing the unit load remains constant or is increased.
- Friction varied directly with viscosity; it was proportional to velocity at lower speeds but varied inversely with velocity at higher speeds [67].

As the surfaces move closer together, the lubricant is squeezed out between them. Some additives, when adsorbed onto the surface, display a molecular orientation perpendicular to the surface that reduces the level of contact and hence lowers the friction. Such products are known as *friction modifiers*. Those additives effective

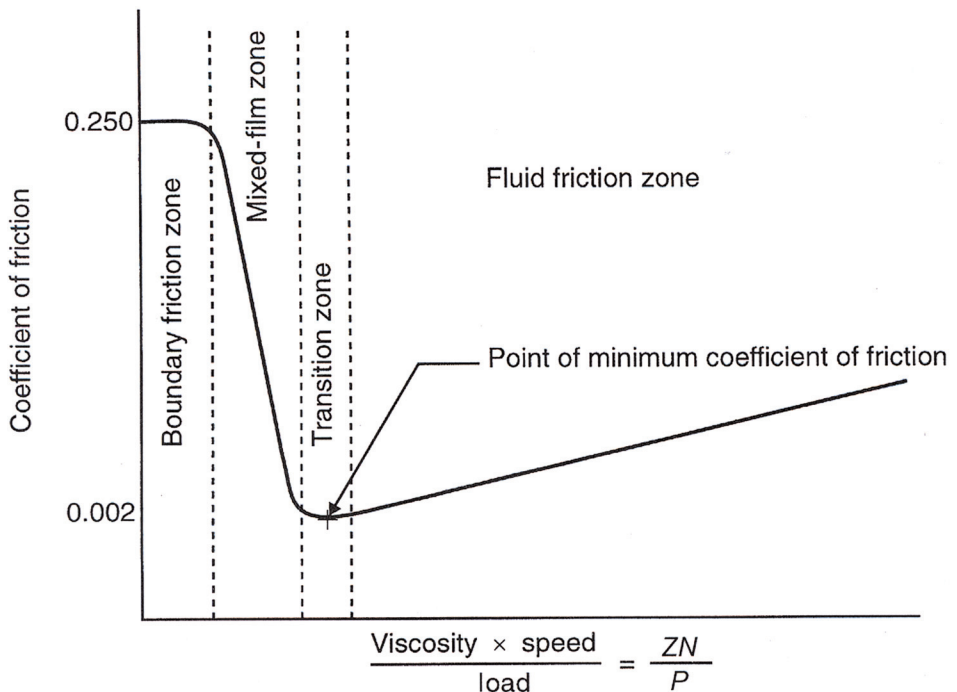


Figure 6 Relationship of coefficient of friction to ZN/P . (From Ref. 67.)

in reducing wear and (usually) friction in the mixed friction zone are called *antiwear additives*, while products effective at reducing wear (and increasing seizure loads) in the boundary lubrication process are known as *extreme-pressure additives*. However, due to the importance of temperature in the lubrication process, it has been pointed out in the past that the latter should perhaps be better described as *extreme-temperature additives*.

The temperature at which an additive reacts physically and/or chemically with the metal or metal oxide surface significantly affects its activity. Each AW/EP additive type has a range of temperatures over which it is active (Figure 7) [68]. The lower end of the temperature range would normally be the temperature at which physical adsorption takes place. This can occur at ambient and higher temperatures depending on the polarity of the additive and the impact on surface energy. The greater the reduction in surface energy, the more strongly absorbed the surface film will be and the greater the likelihood that the additive will remain in place for a chemical reaction with the surface. Additives that are only weakly bound to the surface may desorb as the temperature rises and cease to function further in the wear-reducing process.

As the temperature increases so does the surface reactivity. Fatty acids and esters react at fairly low temperatures to produce metal soaps followed by chlorine-containing compounds (to form chlorides); phosphorus (as phosphates, polyphosphates, and/or phosphides); and, finally, sulfur, which reacts at very high temperatures to form metal sulfides [68].

Chlorine-based additives can be film-forming even at ambient temperatures, but as the temperature rises they become aggressive and, with the release of HCl, can cause significant corrosion. Although the FeCl_2 film has a fairly well-defined melting point at 670°C , the optimum operating temperature is much lower. Klamann [69] indicates that the efficiency of metal chlorides starts to drop above 300°C and that the friction coefficient at 400°C is already a multiple of the optimum value. However, the dry friction coefficient of the chloride film is already substantially lower than that for iron sulfide (Table 4) [70]. The relatively low friction

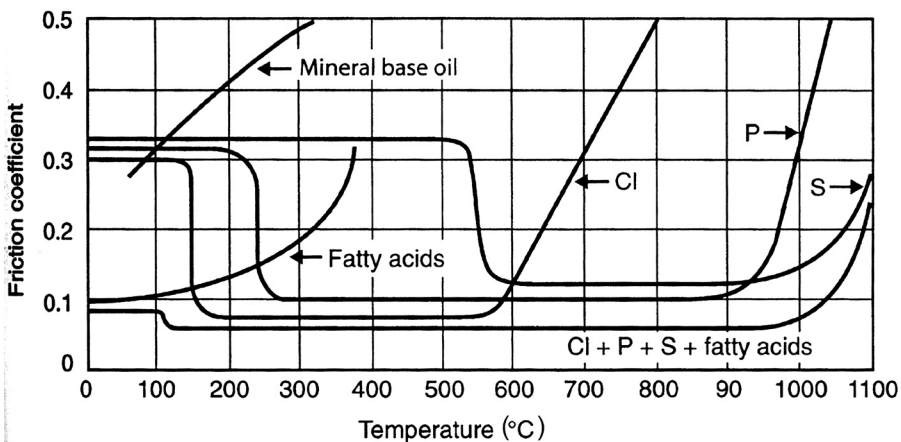


Figure 7 Temperature effect on EP additive activity. (From Ref. 68.)

Table 4 Corrosion Films Formed on Sliding Iron Surfaces

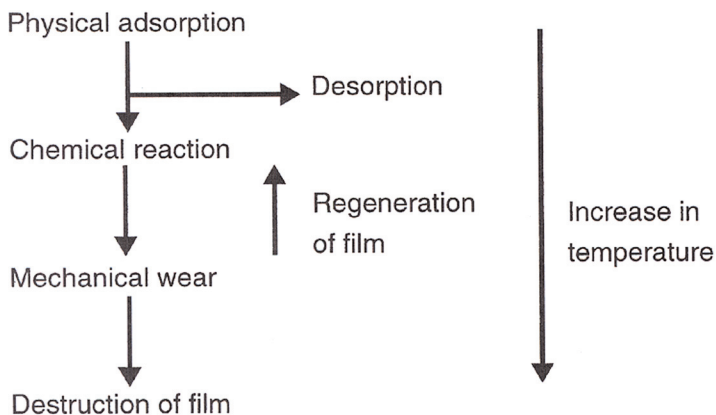
Lubricant type	Nature	Friction coefficient (dry)	Melting point (°C)
Dry or hydrocarbon	Fe	1.0	1535
	FeO	0.3	1420
	Fe ₃ O ₄	0.5	1538
	Fe ₂ O ₃	0.6	1565
Chlorine	FeCl ₂	0.1	670
Sulfure	FeS	0.5	1193

Source: Ref. 70.

associated with this film is probably one reason why chlorinated products are so effective as EP additives. Phosphorus, by comparison, does not react until higher temperatures and then at slower rates. However, the upper temperature limit of ~550°C in an air environment is thought to be a result of the oxidation of the carbon in the film rather than the degradation of a metal soap [71].

The soaps, phosphates/phosphides, chlorides, and sulfides formed on the metal surface were originally considered to produce a lower melting and less shear stable film than that of the metal/metal oxide. This film would cause a smoothing of the metal surface that was then able to support a higher unit loading. This is now thought to be an oversimplified explanation as research has found the EP films to be considerably different to those postulated and without the expected lower shear stability [72]. What it certainly does not consider are additional “subprocesses” of removal of the film by mechanical wear and its possible regeneration in situ by further action of the AW/EP additive (Figure 8).

Since temperature is largely dependent on load, additives that might be effective at high loads may be completely ineffective at low loads (and vice versa). Under such circumstances, therefore, significant wear could occur before the load-carrying properties of the EP additive come into play. In order to minimize this effect,

**Figure 8** Basic processes involved in the mechanism of action of lubricity additives.

additives are often used in combination, resulting in extending the temperature (and load) range over which they are active.

Although single AW/EP additives can be used to meet application and specification requirements, combinations of additives can produce both synergistic and antagonistic effects. The use of mixtures of phosphorus and chlorine or sulfur-containing compounds to extend the temperature range over which a lubricating film is available has already been mentioned. Another example of synergism was reported by Beeck et al. [5], who describe the effect of combinations of TCP and long-chain fatty acids. It was suggested that the use of such mixtures in some way improved the “packing” of the film on the surface and therefore helped to reduce metal contact. Figure 9 [70] in fact shows that combinations of phosphate and fatty acid can result in lower wear rates than either component. Such synergy is useful in that it reduces additive costs and the possibility that the additives might have an adverse effect on product stability, etc. An example of additive antagonism is given in a later section on the use of amine phosphates.

10 INVESTIGATIONS INTO THE MECHANISM AND ACTIVITY OF PHOSPHORUS-CONTAINING ADDITIVES

Many papers have been written about the way in which TCP and other phosphorus-containing compounds work as AW/EP additives. As might be expected, researchers have had differences of opinion. These have probably arisen as a result of the different test conditions found in the wide variety of test equipment developed for measuring wear. For example, different test specimen geometries, surface finish, sliding speeds, and the use of additives with different levels of purity have meant that data have not been strictly comparable.

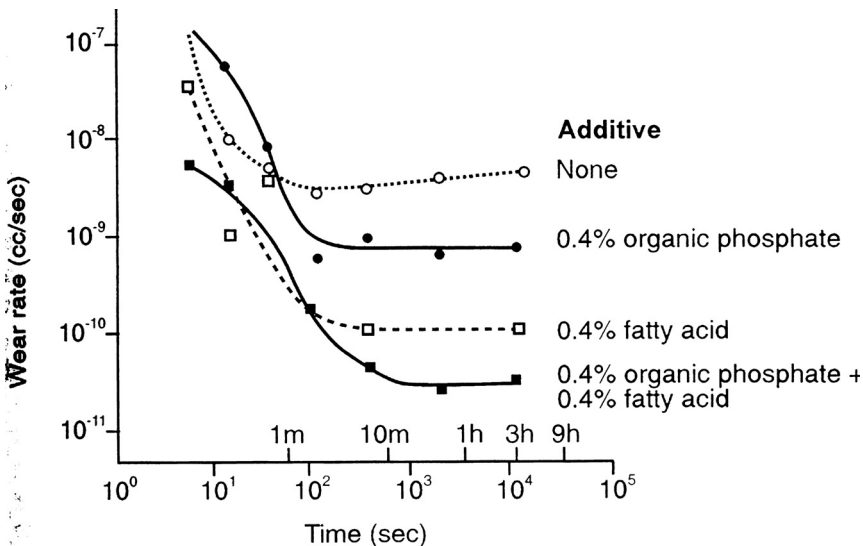


Figure 9 Effect of fatty acid and phosphate ester on wear rate. (From Ref. 70.)

After a brief review of the early development of AW/EP additives, a number of papers exploring the mechanism of action of different phosphorus-based additives are summarized. It is not inclusive, and the results of many other workers could have been mentioned. An additional selection of papers on the topic, is therefore, given in [Appendix 1](#). Some papers evaluate several classes of product; these may be located in sections other than that on neutral phosphates if information on these other structures is limited.

10.1 Early Investigations into Antiwear and Extreme-Pressure Additives

Some of the earliest experiments into the effects of different lubricants on friction were carried out by Hardy in 1919 [73] who noted the superior performance of castor oil and oleic acid. He found that good lubricating properties were closely related to the ability of substances to lower surface energy. A series of papers from Hardy and Doubleday followed in 1922–1923 examining the activity of lubricants under boundary conditions.

In 1920 Wells and Southcombe [74] discovered that the addition of a small amount of a long-chain fatty acid significantly reduced the static coefficient of friction of mineral oil. Bragg postulated in 1925 [75] that long-chain molecules with a polar terminal group were attached to the surface through adsorption of the polar group and that the long hydrocarbon chains were oriented perpendicular to the surface. He also suggested that the formation of films on both the moving surfaces assisted lubrication by sliding over one another, with their long chains being “flattened” as the distance between the surfaces was reduced. However, in 1936 Clark and Sterrett [76] showed that the lubricating film could be up to 200 molecules in thickness but that only the first layer would have the strength to withstand the shearing stresses produced under sliding conditions. They also found that certain ring structures (e.g., trichlorophenol) that were active as “film strength” additives also showed molecular orientation, in this case parallel to the metal surface, and attributed the good load-carrying performance to the ability of the layers to slide over one another. Orientation was not the only factor involved, as compounds with a similar orientation could show a wide difference in performance.

The mechanism and influence of additives on boundary lubrication were first investigated and reported by Beeck et al. [4]. They found that friction was reasonably constant with sliding velocity up to a critical velocity, beyond which there was a significant reduction. Additives were found to reduce the friction at low speeds relative to the base oil alone and also had a significant, but variable, effect on the reduction at different critical velocities. Low critical velocities were found for compounds that were strongly adsorbed and that showed orientation of the surface film. It was recognized that the adsorbed layer is thinner than the roughness of even the best machined surfaces and that high temperatures (or loads) at points of contact would cause decomposition of the molecules with the formation of a high melting corrosion product and an increase in friction. If the surfaces were “highly polished,” then sliding could take place without destruction of the surface film. It was concluded that most of the friction-reducing compounds, principally the long-chain fatty acids, were not able to produce a highly polished surface and, therefore, failed to be effective antiwear additives.

10.2 Neutral Alkyl and Aryl Phosphates

10.2.1 Historical Background

One additive examined by Beeck et al. [5] that was able to reduce both friction and wear was tricresyl phosphate (TCP), a product that was at the time beginning to find widespread commercial use as an AW additive. The authors proposed that TCP acted by a “corrosive” action, preferentially reacting with the high spots on the surface, where surface temperatures are greatest (from metal contact). It was thought that in the reaction, the phosphate ester formed a lower melting phosphide (or possibly an iron/iron phosphide eutectic) that flowed over the surface and caused a smoothing or chemical polishing effect. They also observed that there appeared to be an optimum level of addition of the TCP (1.5%), a conclusion later confirmed by other workers in the field.

Beeck et al. claimed in these papers that their research had produced a better understanding of the antiwear mechanism and enabled more precise distinctions to be drawn between the different types of additives; more specifically that

A wear prevention agent reduces pressure and temperature through better distribution of the load over the apparent surface. If the resulting minimum pressure is still too high for the maintenance of a stable film, metal to metal contact will take place in spite of the high polish. Since in this case the surface of actual contact is relatively very large, seizure and breakdown will follow very rapidly.

The intervention of the war years encouraged German researchers to prepare and evaluate a number of phosphorus compounds as EP/AW additives, principally phosphinic acid derivatives but also acid phosphates [6,7] while other workers [77] continued to investigate the behavior of TCP. The performance of the latter in a white oil was examined, and it was suggested that the additive reacted with steel to form a thin, solid, nonconducting film that prevented seizure by shearing in preference to metal- to metal contacts. The improved behavior of blends of TCP with fatty acids was explained as being due to improved adsorption of the fatty acid on the surface of the chemically formed film.

In 1950 an extensive evaluation of different neutral alkyl and aryl phosphates and phosphites, in some cases containing chlorine and sulfur, was undertaken [78]. The results of this investigation showed that the action of sulfur and chlorine on the surface is to form a sulfide and a chloride film, respectively. In the presence of the phosphorus, mixed films of phosphide/sulfide or phosphide/chloride were formed. The presence of the phosphide was established chemically by the liberation of phosphine in the presence of hydrochloric acid.

Although the concept of phosphide film formation was challenged at this time [79, 80], it remained the generally held theory until the mid 1960s when several papers appeared with data that contradicted this idea. Godfrey [81] pointed out that the experiments that had indicated the presence of phosphide had all been static, high-temperature investigations and none had identified phosphide on a sliding surface lubricated with TCP. He experimented with the lubrication of steel-on-steel surfaces by TCP followed by an examination of the metal surface. This revealed the presence of a white crystalline material, which was shown by electron diffraction measurements to be predominantly a mixture of ferric phosphate, FePO_4 , and its dihydrate, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. Phosphides, if present, were only in extremely small

quantities. Furthermore, a paste made from the dihydrate showed similar factional characteristics to TCP while a paste from iron phosphide showed no significant reduction in friction. Tests also suggested the importance of air to the performance of TCP as tests carried out under nitrogen revealed substantially increased wear. "Pure" TCP was evaluated and, unlike "commercial" material, showed no significant friction-reducing properties!

The presence and role of "impurities" in the activity of commercial TCP was the subject of investigations using radioactive P^{32} [82]. Results suggested the phosphorus-containing polar impurities—not the neutral TCP—were adsorbed onto the metal surface. The P^{32} found in the wear scar appeared to be chemically bound—not physically adsorbed, but the latter process seemed to be the way that the phosphorus was initially made available on the surface. The authors indicated that the impurities resembled acid phosphates (rather than phosphoric acid, which Godfrey had assumed) and carried out wear tests comparing the neutral ester with both an acid phosphate (dilauryl acid phosphate) and also hydrolyzed TCP. They found that lower concentrations of these compounds generally gave equivalent performance to the neutral ester. Of interest was the observation that, while TCP showed no wear minimum in the reported tests (cf. the results given by Beeck et al. [5]), the data on the acid phosphate, an acid phosphite, and phosphoric acid did display such minima.

The work using radioactive P^{32} also allowed a study of the competition between TCP and different types of additives for the metal surface. This was determined by measuring the residual surface radioactivity after wear tests. Table 5 shows the effect of various types of additives on the adsorption of P^{32} from TCP. The lower the number of counts, the greater the interaction between the additive and TCP.

Radiochemical analysis was also the technique used to investigate the deposition of phosphorus on steel surfaces in engine tests [83]. In this study the effect of different types of aryl phosphates [triphenyl (TPP), tricresyl (TCP), and trixylyl (TXP) phosphates] on case-hardened tappets was examined. The results suggested that the efficacy of these additives correlated directly with their hydrolytic stability, i.e., their ability to produce acid phosphates as degradation products. This was confirmed by tests on a series of other phosphates (largely alkyl diarylphosphates), which showed good correlation between antiscuffing performance and hydrolytic stability (Table 6). Examination of the tappet surfaces revealed the presence of aryl acid phosphates on the surface and the absence of phosphides. Adsorption studies of the neutral aryl and acid phosphates on steel surfaces indicated that, while the film of neutral ester could be more easily removed, the adsorption of the acid phosphate was irreversible, suggesting salt formation. These studies led the authors to conclude that the mechanism involved initial adsorption of the phosphate on the metal surface followed by hydrolytic decomposition to give an acid phosphate. This reacted with the surface to give iron organophosphates that then decomposed further to give iron phosphates.

The importance of impurities in determining the level of activity of TCP was confirmed in yet another paper [84]. The composition of impurities in commercial grades of TCP was determined using thin-layer chromatography and analysis by neutron activation. Acidic impurities, probably the mono- and dicresyl acid phosphates, but also small amounts ($2 \times 10^{-4}\%$) of phosphoric acid, were found at 0.1–0.2%, that is, at levels that had previously been shown to produce significant

Table 5 Effect of Various Additives on the Adsorption of P^{32}

Additive concentration (wt %)	Activity (Counts/min)
0.5 % TCP alone	280
+ 2 % barium sulphonate A	0
+ 2 % barium sulphonate B	80
+ 0.1 % rust inhibitor	16
+ 0.5 % diisopropyl acid phosphite	25
+ 0.1 % dilauryl acid phosphate	24
+ 5.5 % acryloid dispersant	82
+ 7.9 % polymeric thickener	78
+ 0.7 % sulphur-chlorine EP additive	120
+ 0.5 % thiophosphate	150
+ 0.5 % 2,2'-methylene -bis(2-methyl,4-tertiarybutyl phenol)	250
+ 0.5 % sulfurized terpene	290

Source: Ref. 82.

Table 6 Correlation Between Antiscuffing Performance and Ease of Hydrolysis (Acid) of Organic Phosphates

Camshaft	Ford Consul (cams phosphated)
Tappet	Ford Consul (nonphosphated)
Camshaft speed	1500 rpm (equivalent engine speed 3000 rpm)
Base oil	SAE 10W/30 oil without EP additive

Additive (0.08 % w added P)	Relative ease of hydrolysis*	Time to scuffing (min) [†] at a spring load of	
		305 lb	340 lb
Benzyl diphenyl phosphate	100	>30	9
Allyl diphenyl phosphate	100	>30	not tested
Ethyl diphenyl phosphate	80	28	not tested
Octyl diphenyl phosphate	50	15	6
Triphenyl phosphate	50	15	5
Tritolyl phosphate	30	8	not tested
2-Ethylhexyl diphenyl phosphate	5	2-3	not tested
None	—	2-3	not tested

Source: Ref. 83.

*Because of the wide range of hydrolytic stability of these compounds, it was not possible to compare the stabilities of all these compounds in the same acid medium. Consequently, an arbitrary scale was drawn up with benzyl diphenyl phosphate assigned a value of 100.

[†]Mean of several tests.

reduction in wear when added to mineral oil. Other impurities ranged from 0.2–0.8%. This latter category was assumed to contain chlorophosphates based on the amount of chloride ion present. The authors commented that the TCP used for the investigation was the best grade available, but even this material contained up to 25% polar impurities. It was thought typical of the TCP used in the wear studies to date and reported in the literature.

Wear tests on TCP, acid phosphates, and phosphites in a super-refined mineral oil and a synthetic ester (di-3-methylbutyl adipate) indicated that relatively small amounts (0.01%) of additive can produce a significant reduction in the wear in mineral oils and that the acidic materials were more active. However, in the polar base stock, where there is competition for the surface, the amount of TCP required to provide a similar reduction in wear is substantially greater. The effectiveness of the alkyl acid phosphates is not significantly reduced in the synthetic ester, suggesting that their polarity (and hence adsorption) is greater than that of the neutral phosphate, the synthetic ester, and its impurities (Table 7). The authors concluded that the activity of TCP was due to the acidic impurities and that the neutral ester acted as a reservoir for the formation of these impurities during the life of the lubricant.

Until about 1969 the theory regarding the production of a phosphate film on the steel surface seemed to be widely accepted. Reports then appeared that suggested

Table 7 Effect of Concentration on Antiwear Properties of Phosphorus-Containing Additives in a Synthetic Ester*

Additive	Concentration (weight %)	Average wear scar diameter (mm)		
		1 kg	10 kg	40 kg
None	—	0.39	0.71	0.91
TCP	1.0	0.38	0.71	0.97
	3.0	0.40	0.64	0.97
	5.0	0.23	0.25	0.78
	1.0	0.57	0.74	—
Hydrolyzed TCP	0.1	0.17	0.25	0.46
	1.0	0.21	0.41	0.84
Dilauryl acid phosphate	0.01	0.19	0.28	0.43
	0.05	0.17	0.28	0.42
	1.0	0.21	0.41	0.84
Diisopropyl acid phosphite	0.02	—	0.72	—
	0.05	0.16	0.25	—
	0.15	—	0.33	—
Phosphoric acid	0.001	0.41	0.69	0.90
	0.01	0.16	0.37	0.50
	1.0	0.38	0.60	0.78

Source: Ref. 84.

*Four-ball wear test conditions:

test time 1 hr
test temperature 167°C
test speed 620 rpm.

the situation was more complicated. One paper [85] examined and compared the corrosivity toward steel, the load-carrying capacity, and the antiwear performance of several phosphorus compounds. Using the hot-wire technique at 500°C [86] followed by an x-ray analysis of the surface films that were produced, the reactivity (or corrosivity) was studied. Perhaps, not surprisingly, the neutral phosphate and phosphite evaluated showed relatively little reactivity with the steel, whereas the acid phosphate and phosphite produced substantially more corrosion. The anomaly was the behavior of a neutral alkyl trithiophosphite, which showed a very high reactivity but low load-carrying ability, suggesting a different mode of breakdown. Analysis of the films formed confirmed the major presence of basic iron phosphate (or principally iron sulphide in the case of the thiophosphite), but small amounts of iron phosphide were also found in all the x-ray analyses of the degradation products. Evaluation of the load-carrying capacity of the additives was found to vary directly with corrosivity except for the alkyl trithiophosphite. The authors surmised from this that the load-carrying capacity of phosphorus-containing additives was not only due to the reactivity of the films but also to the properties of the film that was formed. The relationship between wear and reactivity also varied directly for several of the compounds, but in the case of the neutral phosphite and the alkyl trithiophosphite there is no correlation. This was attributed to the different composition of the film in these cases. In fact, the authors proposed that the main reaction product of the phosphite could be iron phosphide. They suggested that the load-carrying capacity of the films formed by EP additives fell in the following order:

phosphide > phosphate > sulphide > chloride

while the order of antiwear properties was

sulphide > phosphate > phosphide

The first of these sequences is, of course, different to the order in EP activity predicted from the stability of the films formed on the metal surface and from the general perception that phosphorus is less active than either chlorine or sulfur.

A paper by Goldblatt and Appeldoorn [87] cast doubt on the theory that the activity of TCP was due to the generation of acidic impurities. In this study the activity of TCP in different atmospheres and in different hydrocarbon base stocks was examined. The resulting data showed that TCP was much more effective in a low viscosity white (paraffinic) oil than in an aromatic base stock. The aromatics are good antiwear agents and compete with the TCP for the surface. Under these conditions either the iron phosphate reaction products are less stable or perhaps a thinner and less complete layer is produced and is worn away, leading to an increase in corrosive wear. Surprisingly, the antiwear performance of the mixed aliphatic/aromatic base stock was better than either of the components and was not improved by addition of TCP.

The behavior of TCP in different atmospheres focused on the effect of moisture in a wet-air atmosphere and also under dry argon, i.e., in the absence of oxygen and moisture. No significant differences were found in the results indicated above for the different hydrocarbon base stocks. However, in a further series of tests comparing the behavior under both wet and dry air and wet and dry argon in an ISO 32 grade white oil, TCP was shown to have a slight antiwear effect. The exception was in wet air, when it increased wear but also generally showed higher scuffing

loads than when used in dry argon. In a naphthenic oil of similar viscosity, the use of wet air (or wet argon) again resulted in increased wear and exhibited higher scuffing loads. This behavior was also observed with other phosphates and phosphites. The authors suggest that in dry air the TCP film forms very rapidly and metallic contact quickly falls. In dry argon the same thing happens, only at a slower rate. In wet air the film is not as strong, and metallic contact remains high, while in the case of wet argon it does not form at all. "Thus the formation of a protective film is enhanced by oxygen but hindered by the presence of moisture." The observation [81] that air was necessary for the action of TCP did not consider that moisture was present in the air and could have been responsible for the improvement in wear performance.

The previous theory indicating it was necessary for the TCP to hydrolyze to form acid phosphates before it became active was also challenged. Wear tests on standard and very low-acid TCP in dry argon showed no significant difference in activity. It was concluded that TCP was reacting directly with the surface without first hydrolyzing to an acid phosphate and without being preferentially adsorbed at the metal surface.

In 1972 Forbes et al. summarized the current thinking on the action of TCP [88], which indicated that TCP was an effective AW additive at high concentrations independent of the base oil, but at low concentrations was adversely affected by the presence of aromatics. The acidic degradation products have similar properties but show better performance at low concentrations. It was felt that TCP adsorbed onto the metal surface and decomposed to give acid phosphates that reacted with the surface to give metal organophosphates.

The results of further investigations into the effects of oxygen and temperature on the frictional performance of TCP on M-50 steel were published in 1983 [89]. The critical temperature at which friction is reduced as surface temperature rises was measured under different conditions and found to be 265°C in dry air (<100 ppm water) when full-flow lubrication is used; 225°C under conditions of limited lubrication; and 215°C under nitrogen, also with limited lubrication. Analysis of the surface indicated that TCP had reacted chemically at these temperatures, causing a substantial increase in the amount of phosphate deposited (phosphide was not observed). Oxygen was said to be necessary for this reaction, but the suggestion that prior hydrolysis of the phosphate was required could not be substantiated.

The debate regarding the formation of iron phosphate or phosphide as reaction products in the wear mechanism rumbled on into the late 1970s and early 1980s. In 1978 Yamamoto and Hirano [90] carried out scuffing tests on several aryl and alkyl phosphates. The aryl phosphates showed better scuffing resistance, and it was suggested that the alkyl phosphates reacted with the steel surface, forming a film of iron phosphate under mild lubricating conditions, but that the aryl phosphates reacted only slightly until conditions became more severe with the formation of iron phosphide. The implication was that the phosphide (formed as a result of a reaction between the phosphate and the metal surface) acted as a good EP additive but that the iron phosphate had only AW activity. Surface roughness measurements showed a polishing action for the aryl phosphates (particularly for TCP) but not, under these conditions, for the alkyl phosphates.

The concept of corrosive wear and of phosphates as chemical polishing agents as expressed by Beeck et al. [5] was examined by Furey in 1963 [91]. In his work

the surfaces of difference roughness were prepared and friction measurements made when in contact with a solvent refined oil under different applied loads. In tests on an additive-free oil (unfortunately, no information was available on the sulfur or aromatic content), it was found that friction, in addition to being load-dependent, was low for highly polished surfaces and rose with increasing roughness up to a roughness of about 10 microinches. At about this roughness the percentage metal contact was also found to be at its maximum but decreased thereafter. The explanation given for this was that with increasing roughness, the distances between the peaks and troughs increase but the peaks become flatter. The flatter the peak, the better the load-carrying, while the deeper troughs allow for a greater reserve of oil available locally for lubrication and cooling. When several AW/EP additives were evaluated in the oil, it was found that, although there was a reduction in surface roughness, it was less than that found by the oil alone! Furthermore, at low loads, TCP was able to reduce metal contact significantly but had no effect on surface roughness. At moderate to high loads, while still reducing metal contact the surface roughness was increased. The author concluded that TCP was not acting via a polishing action.

In 1981 Gauthier et al. [92] looked again at the wear process and film formation. They categorized the process into three wear phases: an initial, very rapid phase followed by a medium wear rate and finally a slow wear phase. In the rapid wear phase a brown film was formed that, on analysis, was found to be a mixture of ferrous oxide and phosphate. A blue film, which is formed as the wear rate slows (and the surface becomes smoother), contained no iron and was described as a polymeric acid phosphate. (No mention was made of the "white crystalline film" Godfrey reported.)

When both films were removed and the roughness of the underlying surface was measured, it was found that the surface below the brown film was very smooth. The surface under the blue film was much rougher and some 1000Å thicker. The authors suggested that the smooth surface was the result of polishing arising from corrosive wear. They concluded that in the first phase of wear, a corrosive wear process is involved because of the presence of ferrous phosphate on the surface. When a "critical value" for the surface coverage by the phosphate has been achieved, the organic phosphoric acids produced by the decomposition of TCP polymerize to form a polyphosphate. As a result, in the last two wear phases, "the wear of metal is almost completely replaced by the wear of the additive." In this way the disparate observations of TCP behavior (polishing versus increased surface roughness) could be related and combined.

The presence of polyphosphate was also noted by Placek and Shankwalkar [93] when investigating the films produced on bearing surfaces by pretreatment with phosphate esters. Tests were carried out on 100% phosphates and also on their 10% solutions in mineral oil, the latter condition because the combination had been reported to provide better wear protection than the individual components alone, apparently by the formation of a "friction polymer" [94,95]. Phosphates chosen for the work included both aryl and alkyl types. Analyses of the films formed by immersion in the phosphates at 250°C revealed the presence of a high level of carbon together with iron phosphate/polyphosphate and a small amount of phosphide. At 300°C the hydrocarbon had all but disappeared and no phosphide was detected. The films formed by the mineral oil solutions were mainly hydrocarbon-based, but the film formed by the alkyl phosphate was unique in that it contained needlelike

fibers. The effect of the pretreatment on the wear found under four-ball test conditions is indicated in Table 8. The bearings treated with the mineral oil solutions displayed at least as good wear reduction as those treated with the 100% phosphate.

10.2.2 Recent Technical Developments

In 1996 [96] Yansheng et al. reported on the effect of TCP on the wear performance of sulphurized, oxy-nitrided, and nitrided surfaces. A synergistic effect on nitrided and oxy-nitrided surfaces was found, resulting in significant increases in load-bearing capacity while reducing friction and wear, but no improvement was seen on sulfurized surfaces.

A recent application in this brief survey relates to the use of aryl phosphates as vapor-phase lubricants. Although not strictly an additive application, this development has been the focus of most recent analytical studies into the mode of action of these additives, so the conclusions represent the current thinking. Aryl phosphates were chosen for this application because of their high-temperature stability and their ability to provide good boundary lubrication at high temperatures. The initial studies took place with TCP [97] and involved examination of the films formed on tool steel balls and on iron, stainless steel, copper, nickel, tungsten, and quartz wire specimens. (TCP vapor had previously been shown to form tenacious films on graphite, tungsten, and aluminum at temperatures above its thermal decomposition point [98].) Wear tests on tool steel with vapor at 370°C showed low levels of wear even at 0.1 mole percent concentration (Figure 10). An optimum concentration was reached at about 0.5 mole percent. Reaction with the metals indicated above is displayed in Figure 11, which shows that deposition on iron and copper is relatively fast but slow for quartz, nickel, and tungsten. Rates of formation are, of course,

Table 8 Friction and Wear Reduction from Bearing Surface Pretreatment by Phosphate Esters*

Bearing preparation	Average scar diameter (mm)	Improvement (%)	Maximum torque (gf m)	Improvement (%)
Untreated reference	1.00	—	46.1	—
TCP	0.72	28	18.4	60
IPPP	0.75	25	18.4	60
TOF	0.1	19	18.4	60
10% TCP in mineral oil	0.72	28	18.4	60
10% IPPP in mineral oil	0.72	28	15.0	68
10% TOF in mineral oil	0.64	36	19.6	58

Source: Ref. 93.

*ASTM D4172-88

Four-ball wear test conditions:

test time 60 min

test temperature 75°C

test load 40 kgf

test speed 600 rpm

All wear tests performed in 100 solvent neutral paraffinic mineral oil.

IPPP = isopropylphenyl phosphate

TOF = tris-(2-ethylhexyl)phosphate

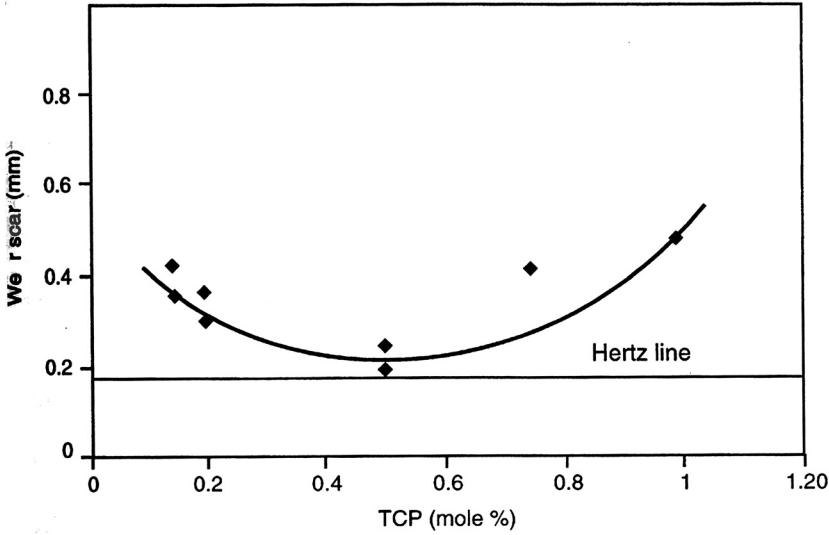


Figure 10 Four-ball wear values at 370°C with vapor lubrication as a function of TCP vapor concentration. (From Ref. 97.)

temperature-dependent, but films are produced up to at least 800°C. Increases in temperature and/or TCP concentration caused an increase in deposit formation.

The use of TCP vapor to lubricate high-speed bearings made from M50 steel at 350°C was examined by Graham et al. in 1992 [99] with excellent results. In fact, the

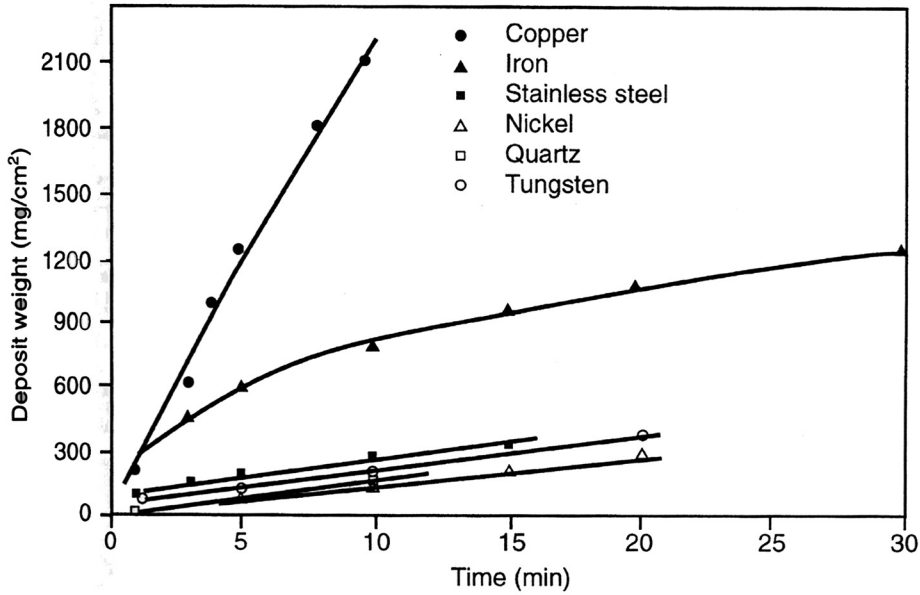


Figure 11 Deposition on various substrates with 1.55% TCP in nitrogen stream at 700°C. (From Ref. 97.)

wear area was smoother than the unused surface. Surprisingly, similar results were found when lubricating silicon nitride surfaces without prior activation. Here, the results were clouded by the transfer of copper to the test specimens, and it was thought that activation could have occurred by reaction of TCP with copper components of the vapor delivery system, which was then deposited onto the ceramic surface. Analysis of the film formed by TCP on a ceramic surface was investigated by Hanyaloglu and Graham [100]. In this case the ceramic was activated by a film (~20 atoms thick) of iron oxide. The presence of TCP at 0.5% in nitrogen or air at 500°C gave a friction coefficient of 0.07 and produced a polymer containing mainly carbon, oxygen, and a small amount of phosphorus with a molecular-weight range of 6,000 to 60,000 g/mole.

A combination of vapor and mist lubrication has also been evaluated in the lubrication of gas turbine bearings [101]. The data indicated that organophosphates worked well with ferrous metal due to the rapid formation of a predominantly iron phosphate film. This was followed by the development of a pyrophosphate-type film over the iron phosphate. As long as iron was present, the organophosphates worked well, but continued production of the phosphate/pyrophosphate film reduced access to iron and eventually led to surface failure. Morales and Handschuh [102] reported to development of a solution to this problem in which the phosphate contained a small quantity of ferric acetylacetonate. Evaluation of this solution in comparison with the pure phosphate showed that the iron salt enabled a phosphate film to be successfully deposited onto an aluminum surface, which the pure phosphate is unable to do. (Phosphates are known not to wet the surface of aluminum.) Vapor/mist lubrication of a gearbox using pure phosphate was compared with the performance of the phosphate containing the iron salt; a significant improvement in scuffing performance was noted. This was enhanced when the mist was directed onto the teeth immediately before contact. Evaluation of the surface film on the gear teeth revealed no phosphorus when the pure phosphate was tested but showed the presence of "fair amounts" of both iron and phosphorus when using the soluble iron salt.

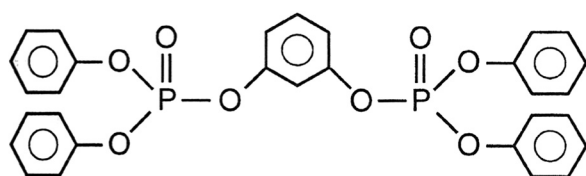
A recent study of the mechanism of film formation by aryl phosphates [103] involved examining the reaction of phosphates with metal in the form of foil or powder and also with various metal oxides in different oxidation states. The tests were carried out in both oxygen-rich and oxygen-depleted environments and revealed that the reactivity of both the commercial grade of TCP, as well as the pure isomers, increased with steel and other metals with increasing oxidation state of the metal/oxide. In comparison with little or no degradation in the absence of metal/metal oxides, limited degradation took place in the presence of metal, but almost complete breakdown of the phosphate occurred (at the same temperature—in the region of 440–475°C) in the presence of Fe_2O_3 and Fe_3O_4 . The isomeric forms of TCP also displayed different levels of reactivity with tris-orthocresyl phosphate (TOCP), more active than the meta- and para-isomers. The authors indicate that these relativities are consistent with the oxide's free energy of formation; those oxides with the highest free energy of formation show the lowest level of activity, and vice versa. Different types of steel surface also displayed different levels of reactivity, with 316C stainless being the least active.

Surface analysis of the steel specimens used indicated that, depending on whether the metal surface was oxygen-rich or poor, different mechanisms of

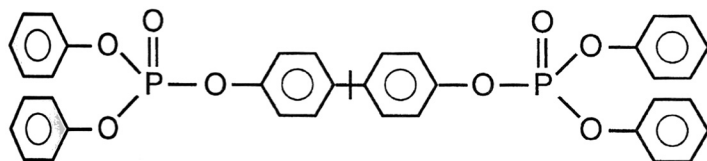
degradation predominate. When excess oxygen was present, the film produced was a polyphosphate with good lubricating properties, whereas a surface with only a thin oxide coating produced iron phosphate, which has poor lubrication properties. No phosphide was found in the surface coating, but an iron/amorphous carbon layer, possibly rich in fused aromatics, arising from the degradation of the aromatic part of the phosphate was found when using the tertiarybutylphenyl phosphate, but not when TCP was examined. Since these aromatics have a planar structure, they may assist with the lubrication by allowing the surfaces to move more easily over one another. However, it is likely that the end result is a composite of the behavior of the polyphosphate and the carbonaceous film, if formed. Indeed the author suggests that the polyphosphate may be acting as a “binder” for the carbon and it is the latter that is providing the lubrication. The proposed mechanism for the formation of the polyphosphate film was thought to involve the cleavage of the C–O bond on one of the pendant groups as the phosphate attaches itself to the surface (presumably via the $\text{P}=\text{O}$ function), eliminating a cresyl radical. This is followed by elimination of another cresyl radical as a second C–O bond breaks and an Fe–O bond is formed. In this way a “lattice of cross-linked PO_3 is formed with the Fe surface.” Wear of the film is not a problem at it appears to be self-healing due to diffusion of Fe ions through the polyphosphate layer to the surface where reaction with phosphate continues. There is no suggestion that hydrolysis of the phosphate is involved.

10.2.3 Recent Commercial Developments

Although the majority of phosphates used as AW/EP additives are relatively low-viscosity products, interest has been expressed in high-molecular-weight materials for aerospace applications, where low volatility is important; for example, high-temperature lubricants for aero-derivative gas turbines and greases for space vehicles. Three products have become commercially available and have been evaluated: an ISO 100 tertiarybutylated phenyl phosphate with low triphenyl phosphate



Resorcinol tetraphenyl bisphosphate



Isopropylidene di-p-phenylene tetraphenyl bisphosphate

Figure 12 Structures of high-molecular-weight phosphate esters.

content; resorcinol tetraphenyl bisphosphate (Figure 12); and isopropylidene di-p-phenylene tetraphenyl bisphosphate (Figure 12). The hydrolytic stability of the resorcinol diphenyl phosphate is relatively poor, but this would not be of major concern for aerospace applications, e.g., in greases. However, this material has been claimed as an antiwear additive for fuels and lubricants [104] while the tertiarybutylphenyl phosphate has been incorporated into an aerospace grease formulation [105].

As part of an assessment of the high-molecular-weight additives for use in high-temperature aviation gas turbine oils, they were compared under coking, four-ball wear, and oxidation test condition [106]. The results are given in Table 9. Although the antiwear performance of the butylated phenyl phosphate is not as good as that of TCP, the reduced impact on deposit formation and magnesium corrosion performance has made it the most promising candidate.

Although much of the recent focus of activity has been on aryl phosphates, there have also been developments with alkyl phosphates. Tributyl phosphate, for example, is now used as an EP additive for EP steam and gas turbine oils used when the turbine is driving a reduction gear [107]. About 1.5% of the additive is used to increase the FZG gear test performance (DIN 51354) from a load stage failure of about 6–8 to 10–11. Again, the neutral nature of the molecule is of advantage in minimizing interaction with other components of the formulation.

An additional application where interest is expressed in alkyl phosphates is in metal working. Due to a desire on environmental grounds to move away from chlorine, the use of phosphorus, particularly in the form of neutral phosphates and their combinations with sulfur-containing additives, is promoted as an alternative [108–111]. As concerns exist about the possible release of phenolic materials into the environment, the alkyl phosphates are perhaps the best suited for this application and are able to provide similar or better performance to the chloroparaffins when correctly formulated. Table 10 shows the drill life and other AW/EP performance in a neat oil of both a low-acid isopropylphenyl phosphate and a neutral alkyl phosphate in

Table 9 The Effect of High-Molecular-Weight Antiwear Additives on the Coking, Wear, and Magnesium Corrosivity of Ester-Based Gas Turbine Oil Formulations

AW additive	Deposit formation* (mg)	Wear [†] (mm)	Magnesium corrosivity ^{††}
Blank—no additive	89	0.655	High
TCP	98	0.40	High
Tris-C ₉ -C ₁₀ alkylphenyl phosphorodithioate	103	0.505	Pass
Tertiarybutylphenyl phosphate	94	0.54	Pass
Resorcinol tetraphenyl phosphate	not determined	0.425	Fail

Source: Ref. 106.

*Fluid held at 300°C for 3 h: method described in paper by Gschwender et al., *Lubrication Engineering*, pp. 20–25, May 2000.

[†]Four-ball wear for 1 h at 40 kg, 600 rpm, and 75°C.

^{††}20 ml sample held for 48 h at 232°C with 1 l/h, air flow.

Additives used at 1% addition in the ester base.

Table 10 A Comparison of the Antiwear/Extreme-Pressure Performance of a Chlorparaffin and an Alkyl or Aryl Phosphate/Active Sulphur Combination in a Simple Oil-Based Cutting Fluid Formulation

Formulation	A	B	C	D
ISO 22 paraffinic oil	92	95.7	96.9	—
Tri-isopropylphenyl phosphate	—	—	—	1.0
Triakyl phosphate	—	—	0.6	—
Active sulfur compound (40% S)	—	4.3	2.5	2.5
Chlorinated paraffin (40% Cl)	8	—	—	—
4-ball wear test (ASTM D4172) (mm)	0.65	—	—	0.43
4-ball weld load (ASTM D2783)				
weld load (kgf)	400	—	—	620
seizure load (kgf)	80	—	—	80
load wear index	51	—	—	104
Pin and V-block (ASTM D3233)				
failure load (1b)	>3100	—	—	2726
Holes drilled to failure (EN24T mild steel at 1200 rpm/0.13 mm per min feed rate)	140	100	280	200

combination with a sulfurized additive when compared with a chlorparaffin. Also in the field of metal working, phosphates have been claimed as components of hot forging compositions [112,113].

11 ALKYL OR ARYL ACID PHOSPHATES

11.1 Nonethoxylated

Although the range in commercial use is limited, acid phosphates are important components of metal-working oils—frequently in combination with chlorparaffins. However, because of environmental concerns associated with the use of chlorinated hydrocarbons, their possible replacement by phosphorus and sulfur compounds has been investigated [68].

Mixtures of mono- and diphosphoric acid esters were compared with a dithiophosphate acid amide in macroemulsions using a variety of EP tests. Performance in drilling and tapping tests (which are regarded as the conditions most closely simulating cutting performance) indicated that, while the amide dithiophosphate gave the best performance, the mono- and diacid phosphates produced levels of performance similar to or better than that of the chlorparaffin without the addition of sulfur carriers.

Traditionally, the acid phosphates in commercial use have high acid numbers (200–300 mg KOH/g). As a consequence, in addition to their use as AW/EP additives,

they are used as corrosion inhibitors [115], and certain structures are promoted as copper passivators [115]. A recent development has been the availability of aryl phosphate-based products that have a relatively low level of acidity (typically 10–15 mg KOH/g) while offering a combination of good AW/EP performance and rust and oxidation inhibition. The multifunctionality of this product type offers opportunities for the simplification of additive packages and use in a wide range of hydraulic and circulatory oils, metal working, and gear applications, while the lower level of acidity reduces the potential for additive interaction and the promotion of foaming, etc.

Increased activity in alkyl acid phosphates has been reported in the patent literature. This arises from the use of long-chain alcohols (C_{16} – C_{18}) to produce an acid phosphate ester mix with a high mono-acid content (preferably greater than 80%:20% mono: diacid ratio) [116]. With this acid distribution it has been possible to achieve lower wear than for the conventional ethoxylated alkyl phosphates with a mono- to di-acid ratio of 60%:40%.

11.2 Polyethylenoxy Acid Phosphates

This is potentially a very large class of compounds. Not only are variations possible in the type of alcohol or phenol chosen but also in the type and degree of alkoxylation. Products of this process were originally claimed to be more active than the nonethoxylated variety, but the latest advances in the latter types reported above [116] suggest this may no longer be the case.

Depending on the choice of raw materials, the finished product may be oil- or water-soluble or water-dispersible. Alkyl and (alk)arylpolyethyleneoxy phosphate ester acids containing less than 55% ethylene oxide (EO) were found to be oil-soluble; products with an EO content of more than 60% were water-soluble as the free acids and as their amine salts, while products with 40–60% of EO were both oil- and water-soluble or dispersible [40]. The free acids are used in oil applications, whereas amine (usually triethanolamine) or metal salts of the acids are used in aqueous applications. The alcohols and phenols initially selected for evaluation were lauryl and oleyl alcohols and nonyl, di-nonyl, and dodecyl phenol. Other raw materials are used today including C_8 – C_{10} alcohols, 2-ethyl hexanol, tridecanol, cetyl-oleyl mixed alcohols, and phenol. Ethoxylation has been used almost exclusively. The products are nonionic surfactants with excellent wetting and emulsification properties, and certain types do not support bacterial growth. They are also good corrosion inhibitors—an important factor in their use in metal-working applications. The higher EO content products tend to produce a heavy and stable foam, and materials containing ~45% EO are therefore preferred for metal-working applications [40].

The effect of the alcohol or phenol and the impact of EO content on the wear behavior in a naphthenic oil can be seen in [Figures 13 and 14](#) [117].

The performance of the product based on oleyl alcohol is interesting in that it does not appear to change with EO content yet is simultaneously capable of producing materials that vary from oil- to water-soluble. However, the four-ball or pin and V-block tests, although widely used as screening tests for the metal-working application, are not considered capable of predicting the performance under cutting conditions. This is confirmed in the paper given in 1995 by Werner et al. [118], which compares the performance of different ethoxylated acid phosphates under a variety of test conditions. Of greater relevance than conventional four-ball or pin and

Acid phosphate esters based on nonionics
containing 23–25% ethylene oxide
Test conditions: 100 rpm; 121°C; 60 min

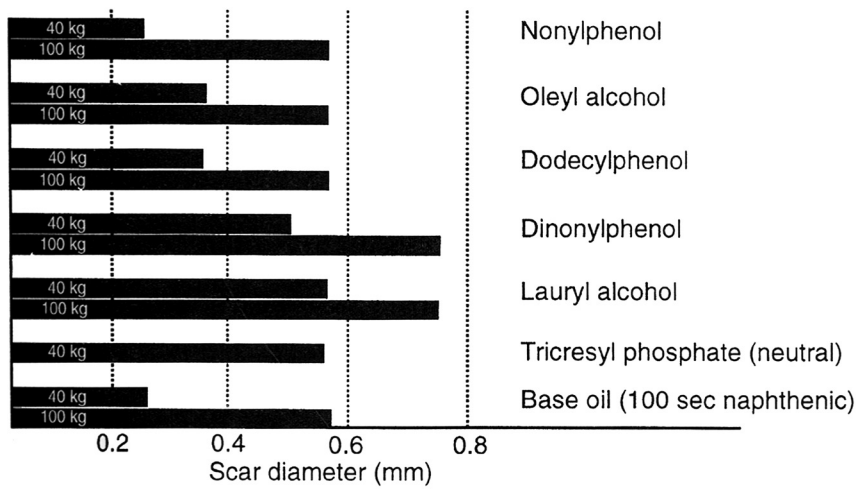


Figure 13 Effect of hydrophobe on wear properties—four-ball scar diameter. (From Ref. 117.)

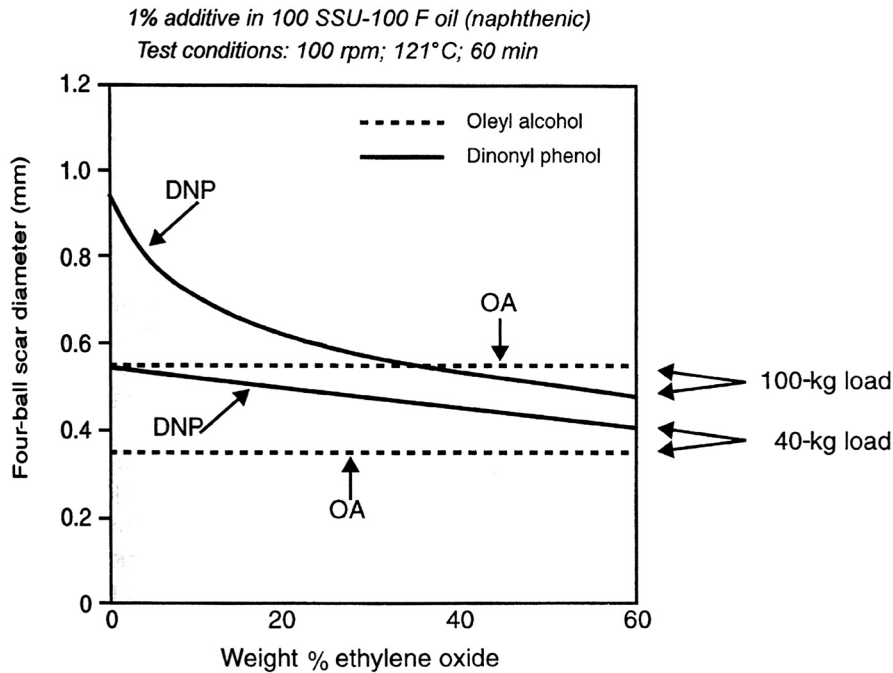


Figure 14 Effect of ethylene oxide content on wear properties. (From Ref. 117.)

Table 11 Ranking of Phosphate Ester Surfactant Results When Wear Tested on Steel in a Water-Based System

Structure	Rankings					HLB value
	Pin and V-block	4-ball	Tapping torque	Total	Overall	
Butane diol + 6 EOs	15	15	13	43	15	—
C ₈ –C ₁₀ alcohol + 6 EOs	8	7	6	21	6	11.5
C ₉ –C ₁₆ alcohol + 5.5 EOs	4	1	4	9	1	13
C ₁₂ alcohol + 6 EOs	1	12	7	20	5	12
C ₁₂ alcohol + 9 EOs	7	5	14	26	9	14
C ₁₂ alcohol + 12 EOs	5	8	12	25	7	15
C ₁₃ alcohol + 4 EOs	13	10	15	38	14	9.7
C ₁₃ alcohol + 6 EOs	9	6	10	25	8	11.5
C ₁₃ alcohol + 10 EOs	2	9	5	16	4	14
C ₁₈ alcohol + 4 EOs	6	4	2	12	2	12
Phenol + 6 EOs	12	13	3	28	11	15.4
Nonyl phenol + 6 EOs	14	3	9	26	10	8
Nonyl phenol + 4 EOs	10	2	1	13	3	11
Nonyl phenol + 9.5 EOs	11	11	8	30	13	13
Dinonyl phenol + 5 EOs	3	14	11	28	12	9

Source: Ref. 118.

EO = unit of ethylene oxide.

V-block tests are actual cutting or tapping-torque tests. The results are given in Table 11, which shows that (1) products with a hydrophilic-lipophilic balance (HLB) value of 11 to 12 give the best results and (2) in general, the farther the value deviates from this, the worse the results become. Unfortunately, no studies appear to have been made on the nature of surface film deposited on the metal, but the adsorption mechanism indicated previously is probably still valid.

12 AMINE SALTS OF ACID PHOSPHATES

One amine phosphate that appeared in the patent literature as early as 1934 as a corrosion inhibitor for aqueous systems (and is still occasionally used) is triethanolamine phosphate [119]. Formed by the neutralization of phosphoric acid with triethanolamine, this product was a widely used corrosion inhibitor for automotive antifreeze formulations for many years [120].

In 1970 Forbes and Silver [121] reported on their work investigating the effect of chemical structure on the load-carrying properties of different phosphorus compounds. In this case the structures under review were di-*n*-butylphosphoramidates, amine salts of di-*n*-butyl phosphate, and derivatives of dialkylphosphinic and alkylphosphonic acids. The results indicated that the phosphoramidates were more effective load-carrying additives than the neutral phosphates, TBP, and TCP, but less active than the amine salts of di-*n*-butyl phosphate.

The evaluation of the series of dialkylphosphinic and alkylphosphonic acid esters indicated that the AW performance related directly to the strength of the acid

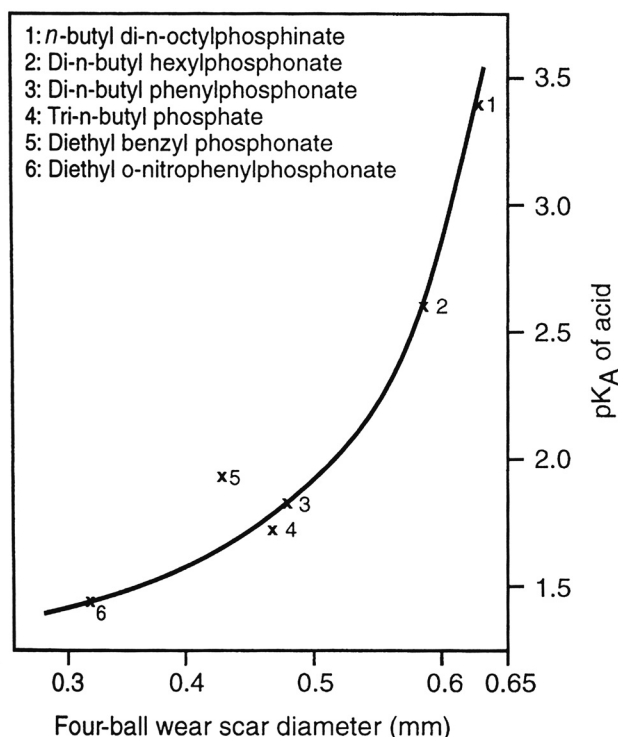


Figure 15 Effect of acid strength on antiwear performance. (From Ref. 121.)

(Figure 15), suggesting that adsorption through the polarity of the ester group was an important step in the process.

In addition to the work carried out in hydrocarbon base stocks, some testing was also performed in a synthetic ester. This fluid enabled a comparison to be made of tetra-alkylammonium salts of dibutylphosphate (otherwise insoluble in mineral oil) which displayed the best AW/EP properties of all the amine phosphates tested (Table 12). The authors suggested this was probably due to the stability of the ions.

A further study of the mechanism of amine phosphates [122] by Forbes and Upsdell appeared in 1973. Adsorption/reaction studies of dibutyl and di-2-ethylhexyl phosphates with either *n*-octylamine or cyclohexylamine and iron powder showed that both the amine and the acid phosphate were adsorbed onto the metal surface and that the rate and extent of their adsorption/desorption varied with chemical structure. The higher the solubility of the iron-phosphate complex formed, the greater was the likelihood of desorption. Further, good AW performance depended on high phosphate and amine adsorption and retention of the phosphate moiety on the surface.

The conversion of a dialkyl acid phosphite to an amine phosphate and the use of the mixed product as a multifunctional AW/EP additive, antioxidant, and corrosion inhibitor with improved metal passivation properties were claimed in 1997 [123].

An amine salt and TCP were studied as AW agents for different synthetic esters by Weller and Perez [124] and compared with a sulphurized hydrocarbon. The neutral ester (TCP) generally showed an increase in wear at 1 % levels before reducing,

Table 12 Four-Ball Test Results of Various Amine Dibutyl Phosphates in Diisooctyl Sebacate

(BuO) ₂ PO ₂ NR ¹ R ² R ³ R ⁴	Extreme-pressure test			Antiwear test		
	MHL	WL	ISL	WSD (mm) after		
	(kg)	(kg)	(kg)	30 min	45 min	60 min
<i>n</i> -C ₄ H ₉ NH ₃	40.5	130	125	0.38	0.38	0.36
<i>n</i> C ₆ H ₁₁ NH ₃	40.0	130	115	0.37	0.38	0.39
PhNH ₃	43.6	140	120	0.37	0.38	0.39
[<i>n</i> -C ₄ H ₉] ₂ NH ₂	34.8	140	100	0.26	0.27	0.33
[<i>n</i> -C ₄ H ₉] ₃ NH	37.4	150	110	0.37	0.38	0.42
[<i>n</i> -C ₄ H ₉] ₄ NH	54.4	150	150	0.25	0.25	0.26
[CH ₃] ₂ [<i>n</i> -C ₈ H ₁₇] ₂ N	56.1	165	165	0.30	0.35	0.40
None	18.6	120	55	0.57	0.61	0.64
Tricresyl phosphate	19.8	110	60	0.31	0.33	0.35

Source: Ref. 121.
% additive = 4 Milliatoms of P/100 g of fluid.

while the amine salt displayed no such maxima and rapidly reduced wear to very low levels. Friction coefficients were also consistently lower with the amine salt.

Kristen [125] reported the effect of additive interaction between amine phosphates and a phosphorothionate. The additives were evaluated under FZG gear test conditions (DIN 51354); the results showed that the additives respond differently in nonpolar and polar base stocks, specifically a polyalphaolefin and a synthetic ester (Figures 16 and 17). In the synthetic hydrocarbon base, a level of 0.75% amine phosphate and 0.25% phosphorothionate (or perhaps 0.5% of each) provided a borderline FZG 12 load stage pass/fail. In comparison, 0.75% of amine phosphate ester and 1% of phosphorothionate were required to achieve the same level of performance in the ester. Monitoring the response of additive combinations not only reveals the most cost-effective mixtures but also any antagonisms between additives, as were found here at higher additive levels in the ester base. Such information is invaluable to formulators when trying to meet specification requirements and ensuring that the performance level is consistently above the minimum limit.

Amine salts, e.g., triethanolamine salts of alkyl and arylpolyethyleneoxy acid phosphates, are widely used in metal-working applications. Some of these products are commercially available but are also produced in situ in metal-working formulations when the pH of the product is adjusted by the addition of base to ensure the product is alkaline in use. This is to avoid corrosion and minimize skin irritation.

13 NEUTRAL ALKYL AND ARYL PHOSPHITES

13.1 Use as AW/EP Additives

The earliest known reference to the evaluation of phosphites as AW/EP additives is in a 1950 paper by Davey [78]. As a result of these investigations, which also included a comparison with phosphates and the effect of incorporating chlorine into the phosphate/phosphite molecule, it was found that

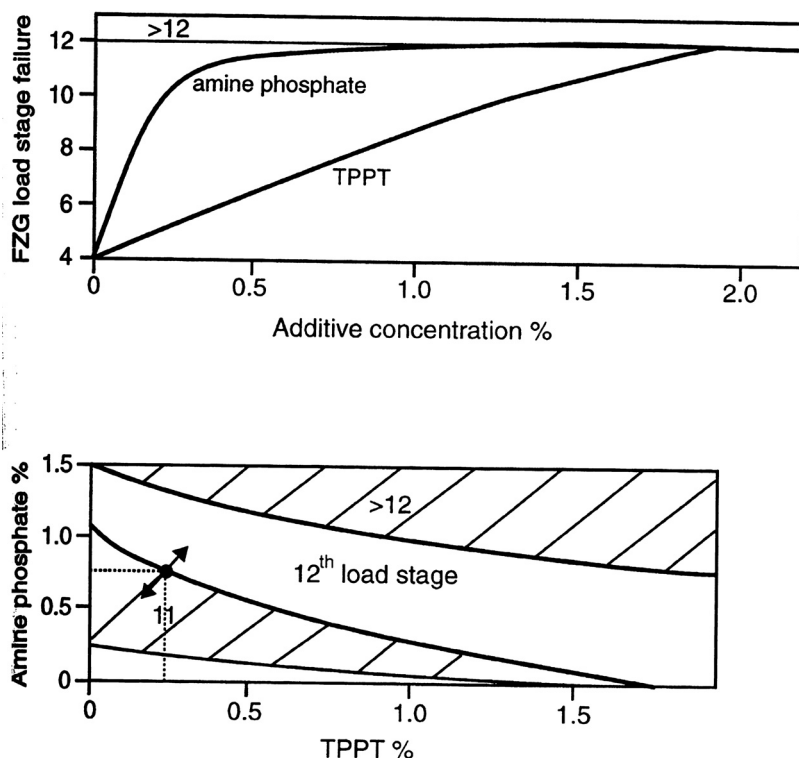


Figure 16 FZG performance of an amine phosphate and triphenyl phosphorothionate separately and in mixtures in an ISO VG 32 polyalphaolefin. (From Ref. 125.)

- Phosphites have superior EP properties to the phosphates, and long alkyl chains are more effective than aryl groups.
- Evaluation of different alkyl and aryl phosphates revealed similar optimum concentrations of between 1–2% with TBP and TXP, as were found in the previous study with TCP [5].
- Polar compounds such as acids or esters improve the lubricating (antiwear) properties of phosphites and phosphates by being strongly adsorbed on the surface.
- The incorporation of chlorine or sulphur into the molecule (or the addition of small amounts of free sulphur) improves the EP properties. Chlorine is more effective when part of an alkyl residue, and when sulphur is added to a P/Cl compound (e.g., a chlorinated phosphite), the EP properties are further improved.

Following the study by Davey a number of patents appeared claiming the use of phosphites in lubricant applications [126–128,130], but it wasn't until 1960 that a further detailed study of the behavior of phosphites, this time by Sanin et al., was published [131]. The study emphasized the correlation of the structure with activity, and the short-chain derivatives were found to be the most active.

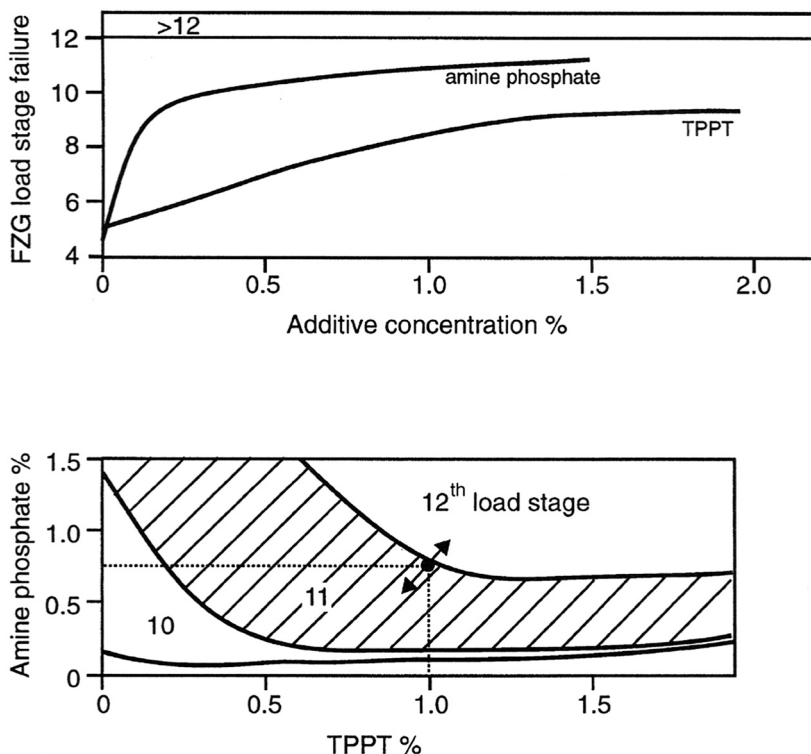


Figure 17 FZG performance of an amine phosphate and triphenyl phosphorothionate separately and in mixtures in an ISO VG 22 pentaerythritol ester. (From Ref. 125.)

In 1993 Ohmuri and Kawamura carried out fundamental studies into the mechanism of action of phosphite EP additives [132]. They found that initial adsorption rates of phosphorus-containing esters depended largely on the existence of -OH and -P=O bonds in the structure. The extent of adsorption was influenced by the hydrolytic stability of the esters, and this process was found to occur through reaction with water adsorbed onto the iron surface. Adsorption of the phosphates varied depending on the degree of esterification; triesters were adsorbed after being decomposed hydrolytically to monoesters, whereas diesters were adsorbed without hydrolysis. Phosphite esters eventually hydrolyzed to “inorganic acid” regardless of the degree of esterification, followed by its adsorption and conversion to the iron salt. It was suggested that the adsorbing and hydrolyzing properties of the esters depended on the arrangement of the molecules physisorbed onto the surface.

Evaluation of a range of alkyl phosphites as EP additives in gear oils was reported by Riga and Rock Pistillo [133]. The most effective products were those with short chains, particularly dibutyl phosphite, which resulted in a wear layer of $>1000\text{\AA}$ and the formation of both iron phosphate and phosphide. Other phosphites formed only traces of phosphide, and as the chain length increased, the resulting film became thinner and contained less phosphorus, possibly due to steric hindrance. Long-chain (C_{12}) alkyl phosphites have also been claimed as AW additives for aluminum rolling oil [134] and, in fact, are still used in metal-working applications.

In view of the work carried out on the use of phosphates as vapor-phase lubricants, an investigation into the effect of phosphites on the frictional properties of ceramics on ceramics and ceramics on metal surfaces was carried out in 1997 [135]. The phosphites (and other additives evaluated) had no effect on ceramic-on-ceramic friction; in fact, short-chain phosphites significantly increased friction. When several types of metal were slid against oxide ceramics, the alkyl phosphites were found to lower the friction for each metal except copper. Apparently, the reaction products between copper and the phosphite had adhesive properties and increased friction.

The decomposition of trimethylphosphite on a nickel surface was also studied in order to obtain insight into the initial steps in the decomposition of phosphates when used as vapor-phase lubricants [136]. The main breakdown path is cleavage of the $-P-O$ bond to yield the methoxy species, which then degrades to CO and H_2 or reacts with the nickel surface. Following heating to 700°K, the surface loses adsorbed species other than phosphorus, which is seen as a simple way for the controlled deposition of phosphorus onto a metal surface.

13.2 Use as Antioxidants for Lubricating Oils

In addition to their use as AW/EP additives, neutral (and acid) phosphite esters have long been used as antioxidants or stabilizers for hydrocarbons. They were originally introduced as stabilizers for rubber and thermoplastics. Trisnonylphenyl phosphite, for example, was first used to stabilize styrene-butadiene rubber in the early 1940s; this was shortly followed by patents claiming phosphates as antioxidants for lubricants, e.g., [49,127,128,137,138].

Phosphites function as decomposers of hydroperoxide, peroxy, and alkoxy radicals (3.19–3.21) rather than eliminating the hydrocarbyl free radicals formed in the chain initiation process. They also stabilize lubricants against photodegradation [139].



This behavior as “secondary” antioxidants by destroying the hydroperoxides, etc. formed in the chain propagation process results in their use in synergistic combination with those antioxidants types that are active as radical scavengers in the initiation process; for example, the hindered phenols and aromatic amines [140–144].

Phosphites are useful additives because of their multifunctionality. However, while they are still used as antioxidants in hydrocarbon oils, their relatively poor hydrolytic stability and the formation of acidic compounds which could affect the surface active properties of the oil have prompted the introduction of “hindered” phosphites with better stability: e.g., tris-(2,4-ditertiarybutylphenyl) phosphite or

tris-(3-hydroxy-4,6-ditertiarybutylphenyl) phosphite; where solubility permits, cyclic phosphites, e.g., based on pentaerythritol such as bis-(2,4-ditertiarybutylphenyl) pentaerythritol diphosphite (Figure 18). These types are claimed as stabilizers or co-stabilizers for lubricating oils [145–148].

Table 13 [147] illustrates the significant improvement in oxidation stability shown by such blends.

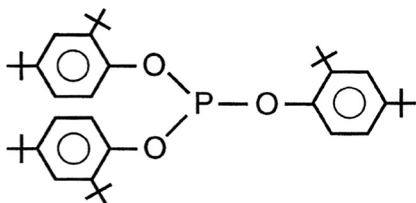
In common with most other types of phosphorus-containing products, neutral (and acid) phosphites have also been claimed as corrosion inhibitors [149,150].

14 ALKYL AND ARYL ACID PHOSPHITES

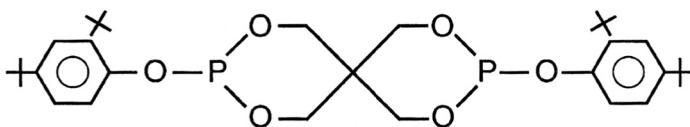
As might be predicted from the behavior of the other types of phosphorus-containing additives, the acid phosphites have good AW/EP properties; the nonylphenyl acid phosphite is particularly effective [151,152]. When used in aviation gas turbine lubricants, the acid phosphites were sometimes formulated in combination with neutral phosphates (TCP); blends of the two products showed synergy even when the amount of the phosphite was very low [153]. The acid phosphites are also claimed to be corrosion inhibitors [154] and antioxidants [48,155,156].

The effect of structure on the antiwear and load-carrying properties of dialkyl phosphites was studied by Forbes and Battersby [157] in a liquid paraffin. Antiwear performance was best with long-chain compounds (Figure 19), while the short-chain (highest phosphorus content) derivatives displayed the best load-carrying performance.

Scuffing behavior, however, appeared to reach a minimum at about a C₈ carbon chain length (Figure 20). This parallels the behavior of the neutral phosphites. Adsorption studies also showed that the phosphorus content of the solution



tris-(2,4-ditertiarybutylphenyl) phosphite



bis-(2,4-ditertiarybutylphenyl) pentaerythritol diphosphite

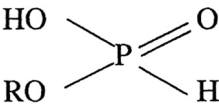
Figure 18 Structures of commonly available hindered phosphites.

Table 13 Antioxidant Synergism Between Hindered Aryl Phosphites and a Hindered Phenol

Base stock	Antioxidant	Oxidation stability	
		% viscosity change	Total acid number increase
1	Hindered phenol (0.5%)	357	11.5
	Hindered phosphite A (0.5%)	438	12.2
	Hindered phenol (0.1%) + phosphite A (0.4%)	8.7	0.01
	Hindered phenol (0.17%) + phosphite A (0.33%)	9.4	0.06
2	Hindered phenol (0.5%)	712	14.2
	Hindered phosphite B (0.5%)	452	10.6
	Hindered phenol (0.1%) + phosphite B (0.4%)	8.1	0.05
	Hindered phenol (0.17%) + phosphite B (0.33%)	8.7	0.03

Source: Ref. 147.
Key: Hindered phenol is tetrakis-(methylene-3,5-di-tert-butyl-4-hydroxy hydrocinnamate) methane.
Phosphite A is tri-(2,4-ditert-butylphenyl) phosphite.
Phosphite B is bis-(2,4-ditert-butylphenyl) pentaerythritol diphosphite.
Test conditions:
IP 48 (modified)
200°C for 24 hr
Air at 15 l/hr in an ISO VG 32 mineral oil.

was depleted in the same order of the load-carrying performance, namely the most active products showed the highest loss from solution. The presence of water increased the uptake of phosphorus from solution. Comparison of the performance of the phosphites against the corresponding acid phosphates revealed that the phosphites had better load-carrying but inferior antiwear behavior (see Table 14). The authors suggest that the activity of the phosphites is due to an initial hydrolysis to produce the following intermediate either in solution or on the metal surface:



This reacts with the iron surface to give an iron salt that was thought responsible for the antiwear properties of the product. Under much more extreme conditions as are

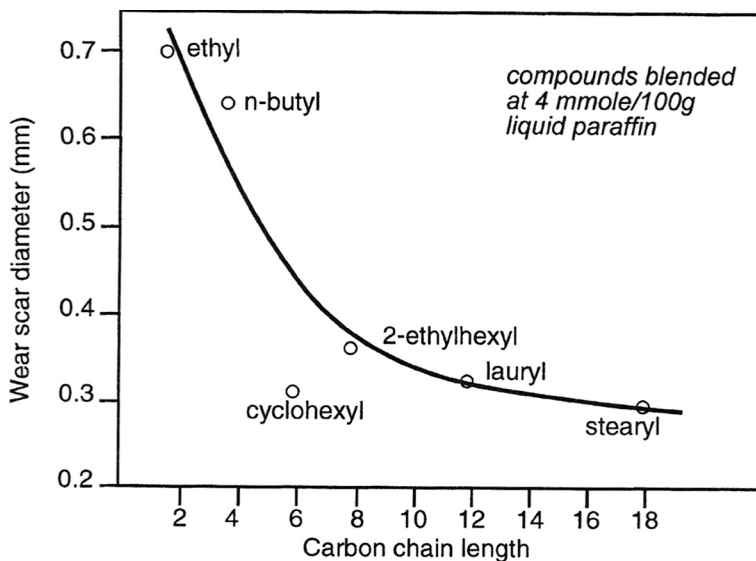


Figure 19 Effect of chain length on the four-ball antiwear performance of dialkylphosphites. (From Ref. 157.)

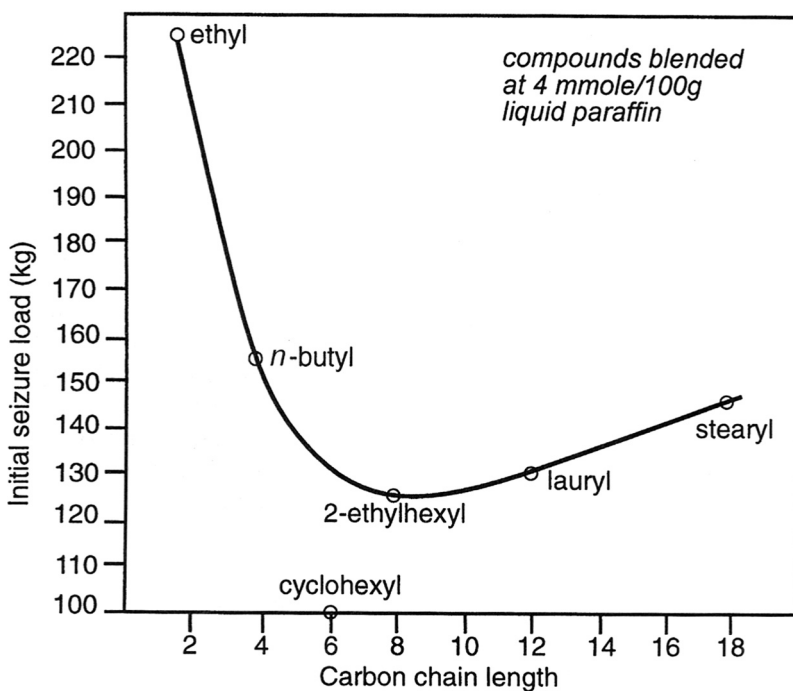


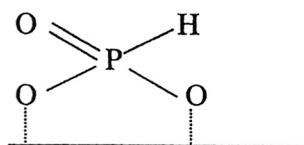
Figure 20 Effect of chain length on initial seizure loads of dialkylphosphites. (From Ref. 157.)

Table 14 Comparison of Load-Carrying Properties of Dialkyl Phosphates and Dialkyl Phosphites at 4 mmol/100 g Base Oil

	Initial seizure load kg	Wear scar diameter (60 min) mm
Diethyl phosphite	225	0.70
Diethyl phosphate	160	0.43
Dibutyl phosphite	155	0.64
Dibutyl phosphate	85	0.42
Di-2-ethylhexyl phosphite	125	0.36
Di-2-ethylhexyl phosphate	80	0.29
Dilauryl phosphite	130	0.32
Dilauryl phosphate	80	0.35

Source: Ref. 157.

found under scuffing, the above salt was thought to decompose further to give the phosphorus-rich layer of the following type:



The authors therefore postulated the reaction scheme given in [Figure 21](#).

15 AMINE SALTS OF ACID PHOSPHITES

In 1975 Barber investigated the four-ball test performance of several long-chain amine salts of short-chain acid phosphites [158], which were found to be very active. Unfortunately he did not investigate the effect of increasing the chain length of the phosphite while reducing the length of the amine. Most of the paper concerns the behavior of a wide range of phosphonate esters (see below).

16 PHOSPHONATE AND PHOSPHINATE ESTERS

A large group of phosphonate esters was prepared by Barber in 1975 [158] and evaluated using the four-ball machine. Although short-chain esters were more effective in preventing scuffing, the most effective products were those containing chlorine. However, even at high levels of chlorine, the performance was still inferior to the amine phosphite reaction products reported above. In comparison with TCP, incipient seizure loads were generally higher, but the weld loads were broadly similar. Unfortunately, there were no direct comparative data under wear test conditions. A limited number of phosphinate esters were prepared and evaluated and found (also by four-ball tests) to give similar performance to the phosphonate esters.

A study of a range of phosphonates by Sanin et al. [159] concluded that their effectiveness depended on their structure and the friction regime, but esters

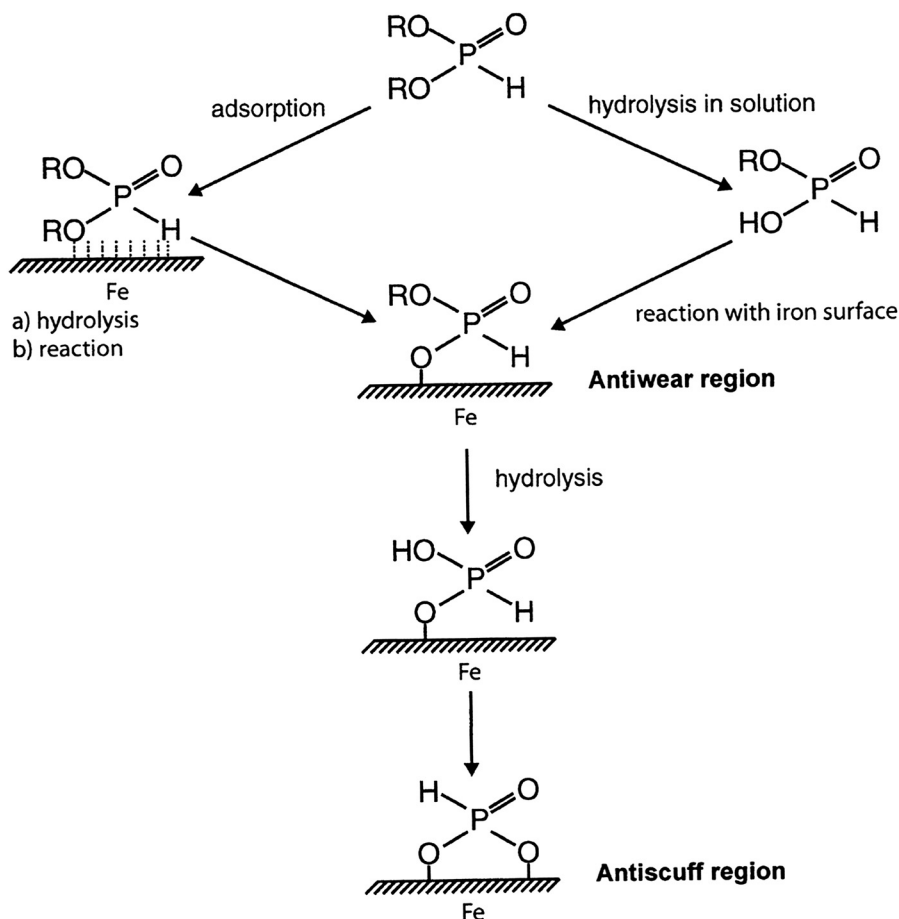


Figure 21 Mechanism of load-carrying action of dialkyl phosphites. (From Ref. 157.)

containing no chlorine had "no effect at either low or high load." A subsequent study by the same authors of the mechanism of activity of phosphonates again suggested the reaction of decomposition products with iron and the formation of a protective layer. Under severe conditions, this layer is removed, resulting in a sudden increase in friction followed by seizure or welding. Studies of the reaction of a dibutyltrichlorophosphonate ($Cl_3CPO(OBu)_2$) indicated that a reaction took place at 405–408°K to give $BuCl$ and an iron-containing polymer. At 413°K this polymer decomposed to give $FeCl_3$, which gave additional protection.

Phosphonate esters, together with pyrophosphonates and their metal or amine salts, have appeared in the patent literature over many years as AW/EP additives. Amine salts of dinonylphosphonate are, for example, claimed in aircraft gas turbine lubricants [160], and dimethyltetradecyl phosphonate has been used in water-based formulations with good pump wear characteristics [161,162]. One of the most recent applications has been in refrigeration compressor oils (e.g., for automobiles) that are compatible with the more ecologically acceptable refrigerants. The reason for their

selection in this application has probably been their good hydrolytic stability in view of the need for a long fluid life [163,164]. Other automotive industry applications for these products include use as friction modifiers, for example in automatic transmission fluids [165], or possibly as detergents in engine oils [166–168] to keep insoluble combustion and oil oxidation products dispersed in the oil.

An alternative method for incorporating phosphorus into dispersants is exemplified in [166]. This method involves reacting P_2S_5 with a sulphurized hydrocarbon, such as sulphurized polyisobutylene, at high temperatures to form a thiophosphorus acid (22). This intermediate is then reacted with propylene oxide to form the hydroxypropyl esters of the phosphorus acid (23). These reactions are shown in Figure 22.

Aminoethane phosphonate co-polymers have also been claimed to provide dispersancy, corrosion protection, and pour point depression [169]. Among other applications mentioned in the literature for these products or their salts in lubricating oils are for the extrusion, cold rolling, and cold forging of aluminum [170], offering improved rust inhibition [171] and antioxidant performance [172].

17 A SUMMARY OF THE PROPOSED MECHANISM FOR AW/EP ACTIVITY OF PHOSPHORUS-BASED ADDITIVES

In attempting to produce an explanation for the activity of phosphorus-containing additives, it is not easy, as explained earlier, to compare the results of the above investigations, because conditions vary from one program to another. No one report evaluates all the different types of additives with the same (high) level of purity under identical test conditions. However, it is possible to draw together some of the more consistent “threads” running through the many papers. One parameter highlighted in past reports (and confirmed by recent observations) is that the presence of oxygen on the metal surface appears to be important for the activity of neutral aryl phosphates. This could perhaps be one of the major reasons why TCP is sometimes found to be inactive. The composition of the film formed on the surface is not yet completely defined, but current work points toward the formation of a self-regenerating polyphosphate layer in which amorphous carbon may be providing the lubrication benefits. The mechanism of formation of the polyphosphate layer and the role, for example, of moisture is not yet clear but appears to be a stepwise process, as follows:

1. The adsorption of the material onto the surface (occurring via the $P=O$ and $P-OH$ bonds in the molecule).

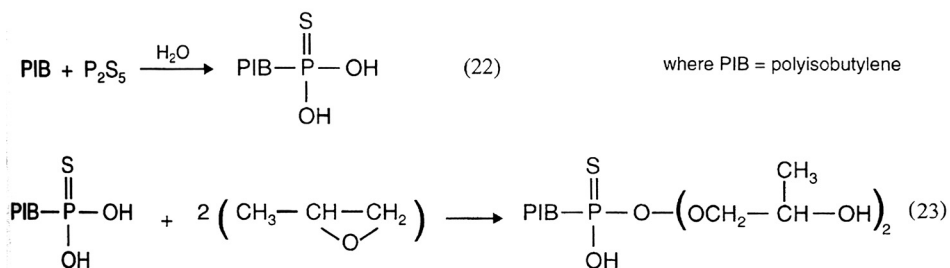


Figure 22 An example of the preparation of a phosphorus-based detergent. (From Ref. 166.)

2. Either the hydrolysis of a -P-OR bond to form -P-OH (probably arising from water on the surface but may also occur in solution) with the formation of acid phosphates/phosphites or, in the case of neutral phosphates, the cleavage of the C-O bond to release an aryl and a residual $\text{-P-O}\cdot$ radical.
3. Either reaction of the -P-OH or -P-(OH)_2 with the metal surface to form an iron salt, possibly followed by further hydrolysis to release the remaining hydrocarbon moieties and reaction of the new -P-OH groups with the surface to form polyphosphate, or the reaction of the residual $\text{-P-O}\cdot$ radical with the iron surface to form a succession of Fe-O-P- bonds leading to the formation of polyphosphate.
4. Products that contain -P-C bonds—e.g., the phosphonates and particularly the phosphinates—are less likely to operate by a mechanism involving hydrolysis, and the stability of the P-C bond might be expected to prevent or delay the formation of the phosphorus-rich surface layer with an adverse effect on EP properties. However, the same stability could result in better friction-modification properties. The fact that phosphinates and phosphonates are active as AW/EP additives suggests that the -P=O bond is also involved in the surface adsorption process, but that either the nature of the surface film may be different or a polyphosphate film is produced as a result of the scission of a -P-C bond.
5. The formation of amine salts results in an increase in activity, possibility as a result of the stability of the ion and improved adsorption on the metal surface.

The mechanism of formation of phosphide, which is reported in many instances, has not yet been clarified.

These conclusions lead, as a broad generalization, to the order in activity and impact on surface chemistry/stability shown in Figure 23.

The above comments are, however, a simplification of the situation. Depending on the length of the alkyl or alkaryl chain, if the iron salts that are formed are soluble in the oil they may desorb from the surface, leading to poor AW/EP performance. Interaction with other surface-active materials will inevitably influence the performance of AW/EP additives, while depletion in use due to oxidation, etc. will also affect performance.



Figure 23 An approximate ranking of the effect of structure on antiwear, extreme pressure, and stability properties of the base stock.

18 MARKET SIZE AND COMMERCIAL AVAILABILITY

The information on the market size for ashless phosphorus-containing AW/EP additives is limited. An approximate total market of about 10,000 tpa is broken down in Table 15.

The above data exclude the use of phosphites as antioxidants in oil applications, which is separately estimated to be between 100 and 200 tpa.

The wide use of phosphorus-containing AW/EP additives is due, in addition to their good lubricity performance, to the following features of value to formulators:

- Ashless
- Low odor, color, and volatility
- Low acidity/noncorrosive (applies to the neutral esters only)
- Low toxicity
- Biodegradable
- Compatible with most other types of additives
- Soluble in a wide range of base stocks, both mineral oil and synthetic, and able to assist the solvency of other additives

Although physical properties for phosphorus-containing additives are not critical, the values for the most widely used types of phosphate ester AW additives are given in Table 16, with TiBP as an example of an alkyl phosphate, TCP as a natural phosphate, and ISO 32 grades of both types of synthetic ester.

The major suppliers of phosphorus-containing lubricant additives are listed in Table 17, and their current applications are summarized in Table 18. Undoubtedly the most important applications for the neutral aryl phosphates are hydraulic, turbine, and general circulatory oils, while almost the entire market for the ethoxylated alkyl and aryl acid phosphates is to be found in metal working. The acid phosphates, acid phosphites, and amine salts of these acidic materials are used in a mixture of metal working, gear oils, hydraulic oils, etc. as indicated in Table 18.

The selection of an AW/EP additive will depend on the specific requirements for the application; for example, whether both AW and EP performance is needed and what levels are required. When this has been ascertained, secondary considerations may be the level of stability required (oxidative or hydrolytic), potential interaction

Table 15 A Breakdown of the Market for Ashless Phosphorus-Containing AW/EP Additives

Product	Market size (tons)
Alkyl phosphates	100
Aryl phosphates	6000
Acid phosphates, ethoxylated alkyl, and aryl phosphates	3000
Phosphites, acid phosphites, dialkyl alkyl phosphonates, and amine salts of acidic products	1000

Table 16 Typical Physical Properties of the Most Widely Used Grades of Phosphorus-based AW Additives

Property		TiBP	TCP	IPPP/32	TBPP/32
Viscosity at 40°C	cSt	2.9	25.0	32.3	33
Viscosity at 0°C	cSt	10.0	1000	990	1500
Specific gravity	20/20°C	0.965	1.140	1.153	1.170
Pour point	°C	< -90	-28	-27	-26
Acid number	mg KOH/g	0.06	0.05	0.05	0.06
Water content	%	0	0.06	0.05	0.05
Phosphorus level	%	11.7	8.3	8.0	8.1
Flash point	°C	155	240	245	255

with other components of the formulation, and the effect on surface-active properties such as foaming. Table 19 attempts to identify the additives that should be given prime consideration when taking these secondary requirements into account. Products are shown that demonstrate better AW than EP activity, and vice versa. However, the boundary between AW and EP performance is not clear-cut and much depends on the application requirements.

19 TOXICITY

Earlier in the chapter we mentioned the past concern regarding the toxicity of phosphorus-containing products, particularly TCP. Today, with increasing focus on the environmental behavior of chemicals, their ecotoxicity is also under scrutiny. As a result of increased legislation, detailed investigations into the toxicity and ecotoxicity have been carried out on both alkyl and aryl phosphate esters, mainly because of their use as industrial and aviation hydraulic fluids and the potential for operator contact in these applications. The results are summarized in recent publications [61, 173]. The alkyl and aryl phosphate esters demonstrate a relatively low order of toxicity and ecotoxicity. One aryl phosphate-based AW/EP additive has, for example, been approved by the German Environment Agency (Umweltbundesamt) for use in rapidly biodegradable hydraulic fluids, products which are eligible for the “Blue Angel” environmental award [174]. In common with many other lubricating oil additives, the ISO 22 and 32 grade phosphates, which are those used principally for additive applications, are classified as marine pollutants, but because they are used at low concentrations they are unlikely to contribute significantly to the finished product’s ecotoxicity.

The past concerns regarding the neurotoxicity of TCP arose when the level of ortho-cresol in the feedstock was ~25% and significant amounts of tri-orthocresyl phosphate (TOCP) were present in the finished product. As a result much work has been carried out to reduce the level of ortho-cresol in raw materials. Mackerer et al. [175] estimate that, as a consequence, the toxicity of TCP now available commercially is 400 times less than that of material available in the 1940s and 1950s. Levels of ortho-cresol today are <0.05%, and the TOCP content can be as low as parts per billion. However, in view of past concerns, usage of TCP is now largely restricted to aviation gas turbine oils, while other industrial applications have

Table 17 Principal Suppliers of Ashless Phosphorus-Containing Lubricating Oil Additives

Producer	Neutral phosphates		Alkyl/aryl acid phosphates		Amine phosphates	Neutral phosphites		Acid phosphites	Alkyl phosphonates
	Alkyl	Aryl	Nonethoxylated	Ethoxylated		Alkyl	Aryl		
Asahi Denka						×	×		
Atochem				×					
Akzo	×	×							
Bayer	×	×							
Ciba Speci. Chem.					×	×	×		
Croda	×		×	×					
Daihachi	×	×							
Dover Chemicals						×	×		
GE Specialty Chemicals						×	×		
Great Lakes Chemicals	×	×				×	×	×	
Johoku Chemicals						×	×		
Libra Chemicals				×					
Octel Starrion			×						
Rhein Chemie	×	×			×				
Rhodia	×	×	×	×	×	×	×	×	×
Sumitomo						×	×		
Uniqema	×			×					
Vanderbilt					×				

Table 18 Principal Applications for Phosphorus-Containing Antiwear/Extreme-Pressure Additives

Application	Triaryl phosphate	Trialkyl phosphate	Amine phosphate	Acid phosphates	Alkyl/aryl phosphites
Automotive					
ATF				✓	✓
Gear oil			✓		
Power steering	✓				
Shock absorber	✓				
Electric motor	✓				
Industrial					
Hydraulic oils	✓		✓		
Gear oils			✓	✓	✓
Turbine oils	✓	✓			
Compressor oils	✓				
Gas oil	✓		✓		
Univ. tractor	✓				
Metal working	✓	✓	✓	✓	✓
Grease	✓		✓	✓	
Way oils	✓				
Circulating oil	✓				
Vegetable oil		✓			
Aircraft					
Piston engine	✓				
Turbine engine	✓				
Grease	✓		✓	✓	

moved to the synthetic phosphates. The cresol-containing products are, in fact, presently the only phosphates to carry a hazard label under existing European legislation.

The toxicity of other phosphorus-containing compounds is less well documented. Drake et al. [176] indicate that dialkyl alkyl phosphonates generally have a low level of acute toxicity, which decreases with increasing chain length, apparently a general observation for these classes of compounds. As with alkyl phosphates, certain short-chain products can be skin irritants. No clues were found to their environmental behavior, but in view of the absence of phenolics and improved hydrolytic stability, it might be surmised that fish toxicity could be good but biodegradability would be inferior to that of the phosphates. Neutral phosphites, particularly the alkyl phosphites, would be expected to have good toxicity and biodegradability behavior, but their ease of hydrolysis, which is the factor assisting the biodegradation, would probably result in poor aquatic toxicity. The future of the nonylphenyl phosphites is uncertain; the U.S. National Toxicology Program currently lists nonylphenol as an estrogen mimic and also as a thyroid disruptor. The acid phosphates, acid phosphites, and their salts, particularly amine salts, are likely to be classified as irritants and, due to their ease of hydrolysis, may again be toxic to aquatic organisms. In all cases it is essential that reference be made to the health and safety information provided by the manufacturer.

Table 19 Guidance on the Selection of Antiwear and Extreme-Pressure Additives

Required characteristic	Good antiwear performance	Good extreme-pressure performance	Combination of AW and EP performance
Nonphenolic additive	Neutral alkyl phosphates; dialkyl alkyl phosphonates	Acid alkyl phosphates; acid alkyl phosphonates and their salts; neutral and acid alkyl phosphites	Possible combinations of neutral and acid phosphates, etc.
Good hydrolytic stability	TXP, dialkyl alkyl phosphonates	Acid alkyl phosphonates and their salts	
Good oxidation stability	Neutral butylated phenyl phosphates	Hindered aryl phosphites	
Low foaming/air release	Neutral phosphates, dialkyl alkyl phosphonates	Neutral phosphites	
Good toxicity/ecotoxicity performance	Neutral isopropylated phenyl phosphates	Acid isopropylated phenyl phosphates	
Multifunctionality, e.g., rust inhibition, antioxidant		Neutral and acid phosphites, acid phosphates	Acid isopropylated phenyl phosphates

20 THE FUTURE FOR PHOSPHORUS-BASED LUBRICATING OIL ADDITIVES

Although chlorine and sulfur have been more widely used than phosphorus in applications where the EP requirement has been very high, the focus on phosphorus has increased today as a result of several industry trends. These are as follows:

- A move toward the use of ashless hydraulic oils. This is largely on two counts: first, as a result of the sensitivity of zinc dialkyldithiophosphates toward moisture and the resulting deposition of zinc oxide/sulfide. This deposit can adversely affect the filterability of the oil and reduce oxidation stability. Second, there is increasing concern regarding the environmental behavior of heavy metals. Regulatory controls, however, are likely to extend further to cover metals like zinc as in the Great Lakes Initiative between the United States and Canada. As the zinc cannot easily be removed from waste at the effluent plant, the alternative method of reducing levels in potential pollutants has been a focus on a reduction in use. More recently, concern has been expressed in certain countries regarding the smell of sulfur arising from the degradation of the ZDTP when the hydraulic oil is used, for example, in elevators [177].
- A move away from chlorine in metal-working applications, particularly in the Far East, led by Japan, largely on environmental grounds. The use of phosphorus-containing additives in combination with sulfur carriers has been shown to be a more than adequate substitute.
- In Europe, new legislation (Directive 2000/76/EC) to be implemented by 2004 will require a substantial reduction in sulfur dioxide emissions from the combustion of waste materials. This will encourage a move to lower sulfur contents in lubricating oils (including metal-working oils) with a probable replacement by phosphorus to restore the level of AW/EP performance.
- Vehicle emissions legislation in the United States, Europe, and Japan now exists which seeks to control and substantially reduce the levels of particulates, hydrocarbons, carbon monoxide, and oxides of nitrogen in the engine exhaust. The engine manufacturers have attempted to meet these requirements by a variety of design changes that impact the composition of oils and fuels in the following ways [178]:
 - The introduction of catalytic converters to oxidize the hydrocarbon and carbon monoxide components to carbon dioxide, and to reduce the nitric oxide to nitrogen, has been very successful in reducing emissions. Most of the residual emissions now occur during the period after ignition, when the catalyst is reaching its normal operating temperature and optimum level of efficiency. Many studies have been conducted into reducing this period to lower emissions still further. Although this has been mostly successful, further progress may be hindered by the formation of a deactivating film on the catalyst surface by the phosphorus from the zinc dialkyldithiophosphate antioxidant and AW/EP additive (ZDTP). It is not clear whether this reduction in performance is due to the presence of phosphorus in any form or results only from the presence of ZDTP. However, the effect to date has been to force phosphorus levels down to 0.1%, with a further drop to 0.08% or even 0.05% under consideration.

- In order to reduce the particulate (soot) levels in exhaust gas, the diesel engines in many passenger cars and trucks need to use particulate filters or traps. These filters have such a high level of efficiency that they also remove the ash-containing residue produced from metallic fuel and lubricant additives. If the filters are not regularly cleaned, they can block with a resulting deterioration in engine performance. The engine builders, however, are trying to preserve or even extend service intervals and consequently are interested in reducing the ash content of the oil. Although ZDTP is not the only source of metals in the oil, a reduction in zinc content will follow automatically from any reduction in the phosphorus content (as long as ZDTP remains in formulations) and will therefore help to reduce engine oil ash content.
- One of the techniques used to remove the soot from the particulate filters (and thereby maintain an acceptable engine back pressure) has been to oxidize the deposited carbonaceous material by nitrogen dioxide (NO_2). This is obtained from the exhaust gas by catalytically oxidizing the nitric oxide (NO). The oxidation of the soot to carbon dioxide effectively reduces filter deposits, and the nitrogen dioxide is such a powerful oxidant that it enables the process to be carried out at relatively low temperatures ($\sim 250^\circ\text{C}$). Unfortunately, the catalyst used to oxidize the NO preferentially oxidizes any sulfur dioxide (SO_2) in the exhaust, thereby reducing the efficiency of the NO conversion. Additionally, the sulfur trioxide (SO_3) formed passes through the trap in the gas phase and is converted there into sulphuric acid by the water in the exhaust. The sulphuric acid (monitored as “sulfates”) contributes, as droplets, to the overall level of particulate emissions and is clearly an undesirable component if the exhaust gas is inhaled. As a result there is pressure to reduce the sulfur content, initially of fuels. In the European Union a limit of 50 ppm maximum sulfur in diesel fuel will be introduced in 2005, with a possible further reduction to 10 ppm in 2011. At these latter levels the engine oil begins to be a significant contributor to the total level of sulfur in the exhaust; not surprisingly, a debate has now arisen regarding the future level of lubricant sulfur. Diesel engine manufacturers have already expressed interest in lubricants with a sulfur level as low as 0.2%—considerably below the current value of $\sim 1\%$.
- Increased emphasis on fuel economy has led to the introduction of direct injection stratified charge gasoline engines. Conventional catalysts do not effectively remove oxides of nitrogen (NO_x) with these “lean-burn” engines and, to overcome this disadvantage, NO_x storage catalysts have been developed in which the oxides are converted to nitrates by reaction with barium sulphate contained in the catalyst coating. When the barium-containing sites become saturated, the engine switches to stoichiometric operation at which temperature the nitrates break down and release the NO_x , thus promoting its reduction via the conventional route of reaction with hydrocarbons and carbon monoxide. Unfortunately, the barium sites then react preferentially with any sulfur oxides present, reducing their efficiency in removing NO_x . As a consequence, there is again pressure to reduce the fuel sulfur content; in the European Union limits

similar to those outlined above for diesel fuel are also to be introduced for gasoline, under an identical timeframe.

- The impact of reducing sulfur and phosphorus in both engine fuels and lubricants is obviously to reduce their antiwear performance. For fuels the use of phosphorus-containing additives has already been proposed to restore the level of performance [179] as there is no conflict with the use of ZDTP. In engine oils the situation is more complicated. If sulfur is reduced, it may be necessary to maintain a significant level of phosphorus in the oil. Additionally the next 5 to 10 years will see the need for friction modifiers in view of the requirements of the new ILSAC GF-4 standard. For the present, however, ZDTP will remain a component of engine oil packages but possibly at reduced levels. In such cases supplementary phosphorus-containing additives may be of value, and some successful studies have already taken place involving a part replacement of ZDTP by phosphorus-based additives [180].
- The current trend toward the use of Group II and III mineral oil base stocks for general industrial applications, with improved oxidative stability but inferior lubricity as a result of the removal of aromatics and sulfur compounds, could encourage the wider use of phosphorus. The lack of competition for the surface, which has previously been shown for TCP in stocks containing naphthenics and aromatics, should result in the increased activity of phosphorus compounds. Their use may also be beneficial due to their ability to aid the dissolution of additives that might otherwise have limited solubility.

21 CONCLUSIONS

Ashless phosphorus-containing additives are available in a wide range of structures and performance. Although most widely used as antiwear and extreme-pressure additives for industrial oils, they can also function as antioxidants, rust inhibitors, metal passivators, and detergents. In some cases the multifunctionality can be found within the same molecule. Their advantageous physical properties—for example, low color and odor and good solubility for other additives—make them attractive components for additive packages. However, while the future looks bright in industrial oil applications in view of current pressure on sulfur and chlorine (mainly as a result of environmental concerns), the potential in automotive applications, both for oil and fuel, remains uncertain and is likely to be the subject of future investigation.

REFERENCES

1. Williamson, Scrugham. *Ann.* 92: 316, 1854.
2. F Vogeli. *Ann.*, 69: 190, 1849.
3. British Patent 446,547 (1936, The Atlantic Refining Co.).
4. O Beeck, JW Givens, AE Smith. On the mechanism of boundary lubrication-I. The action of long chain polar compounds. *Proc Roy Soc A* 177: 90–102, 1940.
5. O Beeck, JW Givens, EC Williams. On the mechanism of boundary lubrication-II. Wear prevention by addition agents. *Proc Roy Soc A* 177: 103–118, 1940.
6. ED Tingle. Fundamental work on friction, lubrication and wear in Germany during the war years. *J Inst Pet* 34: 743–774, 1948.

7. HL West. Major developments in synthetic lubricants and additives in Germany. *J Inst Pet* 34: 774–820, 1948.
8. GD Boerlage, H Blok. Four-ball top for testing the boundary lubricating properties of oils under high mean pressures. *Engng* p. 1, July 1937.
9. U.S. Patent 2,391,311 (1945, C. C. Wakefield).
10. U.S. Patent 2,391,631 (1945, E. I. du Pont de Nemours).
11. U.S. Patent 2,470,405 (1949, Standard Oil Development Co.).
12. U.S. Patent 2,663,691 (1953, The Texas Co.).
13. U.S. Patent 2,734,868 (1956, The Texas Co.).
14. U.S. Patent 2,612,515 (1952, Standard Oil Development Co.).
15. British Patent 797,166 (1958, Esso Research and Engineering Co.).
16. JP Morgan, TC Tullos. The Jake Walk blues. *Ann Int Med* 85: 804–808, 1976.
17. MK Johnson. Organophosphorus esters causing delayed neurotoxic effects: Mechanism of action and structure/activity studies. *Arch Toxicol* 34, 259, 1975.
18. British Patent 683,405 (1952, Shell Refining and Marketing Co.).
19. RJ Greenshields. Oil industry finds fuel additives can help in controlling pre-ignition. *Oil & Gas J* 52(8): 71–72, 1953.
20. RE Jeffrey et al. Improved fuel with phosphorus additives. *Petroleum Refiner* 33(8):92–96, 1954.
21. HD Burnham. The role of tritolyl phosphate in gasoline for the control of ignition and combustion problems. *Am Chem Soc Petrol Div Symp* 36:39–50, 1955.
22. U.S. Patent 3,510,281 (1970, Texaco Inc.).
23. U.S. Patent 2,215,956 (1940, E. I. du Pont de Nemours).
24. U.S. Patent 2,237,632 (1941, Sinclair Refining Co.).
25. French Patent 681,1770 (1929, ICI).
26. U.S. Patent 1,869,312 (1932, Combustion Utilities Corp.).
27. Russian Patent 47,690 (1936, RL Globus, SF Monakhov).
28. U.S. Patent 2,071,323 (1937, Dow Chemical Co.).
29. British Patent 486,760 (1938, Celluloid Corp.).
30. U.S. Patent 2,117,290 (1938, Dow Chemical Co.).
31. AI Shlyakhtenko, PP Lebedev, R Mandel, *NovostiTekhniki*, 20:42, 1938.
32. Russian Patent, 52,398 (1938, AI Shlyakhtenko, PP Lebedev).
33. Canadian Patent 379,529 (1939, Celluloid Corp.).
34. U.S. Patent 2,358,133 (1944, Dow Chemical Co.).
35. British Patent 872,899 (1961, Esso Research and Engineering Co.).
36. French Patent Addn. 89,648 (1967, Etablissements Kuhlmann).
37. British Patent 424,380 (1935-N. V. de Bataafsche Petroleum Maatschappij).
38. U.S. Patent 2,005,619 (1935, E. I. du Pont de Nemours).
39. French Patent 797,449 (1936, E. I. du Pont de Nemours).
40. JPG Beiswanger, W Katzenstein, F Krupin. Phosphate ester acids as load-carrying additives and rust inhibitors for metalworking fluids. *ASLE Trans* 7(4):398–405, 1964.
41. U.S. Patent 3,547,820 (1970, GAF corp.).
42. U.S. Patent 3,567,636 (1971, GAF Corp.).
43. British Patent 1,002,718 (1965, Shell International Research Maatschappij).
44. U.S. Patent 2,381,127 (1945, Texas Co.).
45. U.S. Patent 2,642,722 (1953, Tide Water Associated Oil Co.).
46. British Patent 1,002,718 (1965, Shell International Research Maatschappij).
47. British Patent 1,266,214 (1972, Esso Research and Engineering Co.).
48. U.S. Patent 2,236,140 (1944, Atlantic Refining Co.).
49. U.S. Patent 2,325,076 (1944, Atlantic Refining Co.).
50. Dutch Patent 69,357 (1952, N. V. Bataafsche Petroleum Maatschappij).
51. U.S. Patent 2,653,161 (1953, Shell Development Co.).

52. British Patent 1,247,541 (1971, Mobil Oil Corp.).
53. U.S. Patent 3,600,470 (1971, Swift & Co.).
54. MP Marino, DG Plocek. Phosphate esters in Synthetic Lubricants and High Performance Functional Fluids, 2nd ed. LR Rudnick, RL Shubkin. eds. New York: Marcel Dekker, 1999.
55. DP Evans, WC Davies, WJ Jones. The lower trialkyl phosphates. *J Chem Soc Pt I*: 1310–1313, 1930.
56. U.S. Patent 2,723,237 (1955, Texas Co.).
57. N Canter, private communication, August 2001.
58. U.S. Patent 1,869,312 (1932, Combustion Utilities Corp.).
59. British Patent 1,165,700 (1965, Bush, Boake Allen Ltd.).
60. British Patent 1,146,173 (1966, J. R. Geigy).
61. WD Phillips. Phosphate ester hydraulic fluids, in *Handbook of Hydraulic Fluid Technology*. GE Totten, ed. New York: Marcel Dekker, 2000.
62. U.S. Patent 5,779,774 (1998, KJL Paciorek, SR Masuda).
63. J Tang, Q Cang, X Zong. Preparation and evaluation of phosphorus friction modifiers used in automatic transmission fluids, *Shiyou Lianzhi Yu Huagong* 31(3): 17–20, 2000.
64. Anon. Product review—Lubricant additives. *Ind Lubr and Trib* 49(1):15–30, 1997.
65. AR Lansdown. Extreme pressure additives in Chemistry and Technology of Lubricants, Mortier and Orszulik, eds. New York: VCH Publishers Inc., 1992.
66. Anon. Boundary lubrication. *Lubrication*, 57:1, 1971.
67. RC Gunther. *Lubrication*, Bailey Bros. and Swinfen Ltd., 1971.
68. R Mandakovic. Assessment of EP additives for water miscible metalworking fluids. *J Syn Lubr* 16(1):13–26, 1999.
69. D Klamann. *Lubricants and related products*. Verlag Chemie, 1984.
70. Anon. Fundamentals of wear. *Lubrication* 12(6):61–72, 1957.
71. NH Forster, private communication, July 2001.
72. Anon. Lubrication fundamentals. *Lubrication*, 59(Oct-Dec):77–88, 1973.
73. WB Hardy. Note on the static friction and lubricating properties of certain chemical substances. *Phil Mag* 38:32–49, 1919.
74. HM Wells, JE Southcombe. *Petroleum World* 17:460, 1920.
75. WH Bragg. *Nature*, 115:226, 1925.
76. GL Clark, RR Sterrett. X-ray diffraction studies of lubricants. *Ind Eng Chem* 28(11):1318–1322, 1936.
77. RE Thorpe, RG Larsen. Antiseizure properties of boundary lubricants. *Ind Eng Chem* 41:938–943, 1949.
78. W Davey. Extreme pressure lubricants—Phosphorus compounds as additives. *Ind Eng Chem* 42(9):1841–1847, 1950.
79. RG Larsen, GL Perry. Chemical aspects of wear and friction. *Mechanical Wear*. JT Burwell, ed. American Society for Metals, 1950.
80. O Bitá, I Dinca. Behaviour of phosphorus additives. *Rev Mecan Appl* 8:441–442, 1963.
81. D Godfrey. The lubrication mechanism of tricresyl phosphate on steel. *ASLE Preprint* 64-LC-1, 1964.
82. EE Klaus, HE Bieber. Effects of P impurities on the behaviour of tricresyl phosphate-32 as an antiwear additive. *ASLE Preprint* 64-LC-2, 1964.
83. FT Barcroft, SG Daniel. The action of neutral organic phosphates as EP additives. *ASME Jnl. Basic Eng.* 64-Lub-22, 1964.
84. HE Bieber, EE Klaus, EJ Tewkesbury. A study of tricresyl phosphate as an additive for boundary lubrication. *ASLE Preprint* 67-LC-9, 1967.
85. T Sakurai, K Sato. Chemical reactivity and load carrying capacity of lubricating oils containing organic phosphorus compounds. *ASLE Preprint* 69-LC-18, 1969.

86. FT Barcroft. A technique for investigating reactions between EP additives and metal surfaces at high temperatures. *Wear* 3:440–453, 1960.
87. IL Goldblatt, JK Appeldoorn. The antiwear behavior of TCP in different atmospheres and different base stocks. ASLE Preprint 69-LC-17, 1969.
88. ES Forbes, NT Upsdell, J Battersby. Current thoughts on the mechanism of action of tricresyl phosphate as a load-carrying additive. *Proc Trib Conv* 1:7–13, 1972.
89. OD Faut, DR Wheeler. On the mechanism of lubrication by tricresylphosphate (TCP)—The coefficient of friction as a function of temperature for TCP on M-50 steel. *ASLE Trans* 26(3):344–350, 1983.
90. Y Yamamoto, F Hirano. Scuffing resistance of phosphate esters. *Wear* 50:343–348, 1978.
91. MJ Furey. Surface roughness effects on metallic contact and friction. *ASLE Trans* 6:49–59, 1963.
92. A Gauthier, H Montes, JM Georges. Boundary lubrication with tricresylphosphate (TCP). Importance of corrosive wear. ASLE Preprint 81-LC-6A-3, 1981.
93. DG Placek, SG Shankwalkar. Phosphate ester surface treatment for reduced wear and corrosion protection. *Wear* 173:207–217, 1994.
94. EE Klaus, JM Perez. Comparative evaluation of several hydraulic fluids in operational equipment. SAE Paper No. 831680, 1983.
95. EE Klaus, JL Duda, KK Chao. A study of wear chemistry using a microsample four-ball wear test. *STLE Trib Trans* 34(3):426–432, 1991.
96. Yansheng Ma, Jiajun Liu, Yinshun Wu, Zhengqiu Gu. The synergistic effects of tricresyl phosphate oil additive with chemico-thermal treatment of steel surfaces. *Lub Sci* 9:1:85–95, 1996.
97. EE Klaus, GS Jeng, JL Duda. A study of tricresyl phosphate as a vapor delivered lubricant. *Lub Eng* 45(11):717–723, 1989.
98. L Cho, EE Klaus. Oxidative degradation of phosphate esters. *ASLE Trans* 24(1):119–124, 1981.
99. EE Graham, A Nesarikar, NH Forster. Vapor phase lubrication of high-temperature bearings. *Lub Eng* 49(9):713–718, 1993.
100. B Hanyaloglu, EE Graham. Vapor phase lubrication of ceramics. *Lub Eng* 50(10):814–820, 1994.
101. KW Van Treuren et al. Investigation of vapor-phase lubrication in a gas turbine engine. *ASME J Eng Gas Turbines and Power* 120(2):257–262, 1998.
102. W Morales, RF Handschuh. A preliminary study on the vapor/mist phase lubrication of a spur gearbox. *Lub Eng* 56(9):14–19, 2000.
103. CS Saba, NH Forster. Reactions of aromatic phosphate esters with metals and their oxides. *Tribol Lett.* 12, 2:135–146, 2002.
104. European Patent 0521628 (1992, Ethyl Petroleum Additives).
105. SR Didziulis, R Bauer. Volatility and performance studies of phosphate ester boundary additives with a synthetic hydrocarbon. Aerospace Report TR 95-(5935)-6.
106. L Gschwender, private communication, August 2001.
107. R Ertelt, private communication, September 2001.
108. Japanese Patent 05001837 (1988, Toyota Central Res. & Dev. Lab.).
109. Japanese Patent 02018496 (1990, New Japan Chemical Co.).
110. Japanese Patent 02300295 (1991, Toyota Jidosha & Yushiro Co.).
111. U.S. Patent 6,204,227 (2001, PABU Services).
112. U.S. Patent 5,584,201 (1996, Cleveland State University).
113. Soviet Union Patent 810,767 (1981, Berdyansk Exptl. Pet. Plant).
114. U.S. Patent 5,779,774 (1998, KJL Paciorek, SR Masuda).
115. Metal Passivators, Newsletter No 10, ADD APT AG., June 2000.
116. European Patent Appl. WO 00/37591 (2000, JJ Werner, RL Reiersen, J-L Joye).

117. W Katzenstein. Phosphate ester acids as load-carrying additives and rust inhibitors for metalworking fluids. Proc 11th Int Trib Coll Esslingen, Germany, pp. 1741–1754, 1998.
118. JJ Werner, M Dahanayake, D Lukjantschenko. Relationship of structure to performance properties of phosphate-ester surfactants in metal working fluids. Presented at STLE Annual Conference, Chicago, 1995.
119. U.S. Patent 1,936,533 (1933, E. I. du Pont de Nemours).
120. British Standard 3150, Corrosion-inhibited antifreeze for water-cooled engines, Type A. British Standards Institution, 1959.
121. ES Forbes, HB Silver. The effect of chemical structure on the load-carrying properties of organo-phosphorus compounds. J Inst Pet 56(548):90–98, 1970.
122. ES Forbes, NT Upsdell. Phosphorus load-carrying additives: Adsorption/reaction studies of amine phosphates and their load-carrying mechanism. Paper C-293/73, 277–298, 1st European Trib Cong. London, 1973.
123. U.S. Patent 5,681,798 (1997, LO Farng, WF Olszewski).
124. D Weller, J Perez. A study of the effect of chemical structure on friction and wear, Part 1—Synthetic ester fluids. Lub Eng 56(11):39–44, 2000.
125. U Kristen. Aschnefreie extreme-pressure- und verschleiss-schutz-additive. Additive für Schmierstoffe, WJ Bartz, ed. Expert Verlag, 1994.
126. U.S. Patent 2,722,517 (1995, Esso Res. & Eng. Co.).
127. U.S. Patent 2,763,617 (1957, Shell Dev. Co.).
128. U.S. Patent 2,820,766 (1958, C. C. Wakefield & Co.).
129. GW Crosby, EW Brennan. Am Chem Soc Div Petrol Chem, Preprints, 3(4A): 171, 1958.
130. U.S. Patent 2,971,912 (1961, Castrol Ltd.).
131. PI Sanin et al. Wear 3:200, 1960.
132. T Ohmuri, M Kawamura. Fundamental studies on lubricating oil additives. Adsorption and reaction mechanism of phosphorus-type additives on iron surface. Toyota Chuo Kenkyusho R & D Rebyu 28(1):25–33, 1993.
133. A Riga, W Rock Pistillo. Surface and solution properties of organophosphorus chemical in wear tests. NTAS Ann Conf Therm Anal App 28:530–535, 2000.
134. French Patent 1,435,890 (1996, Albright & Wilson Ltd.).
135. K. Demizu, H Ishigaki, M Kawamoto. The effect of trialkylphosphites and other oil additives on the boundary friction of oxide ceramics against themselves and other metals. Trib Intl 30(9):651–657, 1997.
136. D Ren, G Zhou, AJ Gellman. The decomposition mechanism of trimethylphosphite on Ni (III). Surf Sci 475(1–3):61–72, 2001.
137. British Patent 682,441 (1952, Anglamol Ltd.).
138. U.S. Patent 2,764,603 (1954, Socony Vacuum Oil Co.).
139. M Rasberger. Oxidative degradation and stabilisation of mineral oil-based lubricants. Chemistry and Technology of Lubricants. Mortier and Orszulik, eds. VCH Publishers, 1992.
140. European Patent 0049133 (1982, Sumitomo Chemicals).
141. Japanese Patent 63156899 (1988, Sumiko Junkatsu-Zai).
142. Japanese Patent 2888302 (1991, Tonen Corp.).
143. Japanese Patent 05331476 (1994, Tonen Corp.).
144. Japanese Patent 06200277 (1994, Tonen Corp.).
145. U.S. Patent 4,656,302 (1987, Koppers Co. Inc.).
146. European Patent Appl. 475560 (1992, Petro-Canada Inc.).
147. U.S. Patent 4,652,385 (1987, Petro-Canada Inc.).
148. U.S. Patent 5,124,057 (1993, Petro-Canada Inc.).
149. German Patent 1,271,874 (1968, Hüls Chemicals).

150. German Patent 1,286,675 (1969, Hüls Chemicals).
151. U.S. Patent 3,329,742 (1967, Mobil Oil Corp).
152. U.S. Patent 3,351,554 (1967, Mobil Oil Corp).
153. U.S. Patent 3,321,401 (1967, British Petroleum Co.).
154. U.S. Patent 3,201,348 (1965, Standard Oil Co.).
155. South African Patent 6707230 (V Messina, DR Senior).
156. U.S. Patent 3,115,463 (1963, Ethyl Corp.).
157. ES Forbes, J Battersby. The effect of chemical structure on the load-carrying and adsorption properties of dialkyl phosphites. *ASLE Trans* 17(4): 263–270, 1974.
158. RI Barber. The preparation of some phosphorus compounds and their comparison as load-carrying additives by the four ball machine. *ASLE Preprint* 75-LC-2D-1, 1975.
159. PI Sanin et al. Antiwear additives of the phosphonate type. *Neftekhimiya* 14(2):317–322, 1974.
160. U.S. Patent 3,553,131 (1971, Mobil Oil Corp.).
161. U.S. Patent 4,246,125 (1981, Ethyl Corp.).
162. U.S. Patent 4,260,499 (1981, Ethyl Corp.).
163. European Patent Appl. 510633 (1992, Sakai Chemicals).
164. Japanese Patent 05302093 (1993, Tonen Corp.).
165. U.S. Patent 4,225,449 (1980, Ethyl Corp.).
166. CC Colyer, WC Gergel. Detergents/dispersants. *Chemistry and Technology of Lubricants*. Mortier and Orszulik, eds. VCH Publishers, 1992.
167. Japanese Patent 62215697 (1987, Toyota Res. and Devt.).
168. Czech Patent 246897 (1988, Kekenak).
169. U.S. Patent 3,268,450 (1966, Sims, Bauer and Preuss).
170. Japanese Patent 8126997 (1981, Showa Aluminium Co.).
171. U.S. Patent 4,123,369 (1978, Continental Oil Co.).
172. U.S. Patent 3,658,706 (1972, Ethyl Corp.).
173. MJ Goode, WD Phillips. Triaryl phosphates ester hydraulic fluids—A reassessment of their toxicity and environmental behaviour. *SAE Paper* 982004, 1998.
174. Durad® 310N, Great Lakes Chemical Corp. May 2002.
175. C Mackerer, ML Barth, AJ Krueger. A comparison of neurotoxic effects and potential risks from oral administration or ingestion of tricresyl phosphate or jet engine oil containing tricresyl phosphate. *J Toxicol Environ Health, Part A*, 57(5):293–328, 1999.
176. GL Drake, Jr., TA Calamari. Industrial uses of phosphonates in Role of Phosphonates in Living Systems. R Hildebrand, ed. Boca Raton, FL: CRC Press, 1983.
177. R Dixon. Shell Global Solutions, private communication, November 2001.
178. U.S. Patent 5,630,852 (1997, FMC Corp.).
179. R Mainwaring. Shell Global Solutions, private communication, August 2001.
180. SH Roby, JA Supp. Effects of ashless antiwear agents on valve train wear and sludge formation in gasoline engine testing. *Lub Eng* 53(11):17–22, 1997.

Appendix 1 Additional Literature and Patent References on the Mechanism and Performance of Phosphorus-Containing Additives

1 NEUTRAL PHOSPHATES

- DH Han, M Masuko. Comparison of antiwear additive response among several base oils of different polarities. *Tribol Trans* 42(4):902–906, 1999.
- DH Han, M Masuko. Elucidation of the antiwear performance of several organic phosphates used with different polyol esters base oils from the aspect of interaction between the additive and the base oil. *Tribol Trans* 41(4):600–604, 1998.
- JM Perez et al. Characterization of tricresyl phosphate lubricating films. *Tribol Trans* 33(1):131–139, 1990.
- HM Ghose, J Ferrante, FC Honey. The effect of tricresyl phosphate as an additive on the wear of iron. NASA Tech. Memo, NASA-TM-100103, E-2883, NAS1.15:100103.
- K Weber, E Eberhardt, G Keil. Influence of the chemical structure of phosphoric EP-additives on its effectiveness. *Schmierungstechnik*, 3(12):372–377, 1972.
- H Wiegand, E Broszeit. Mechanism of additive action. Model investigations with tricresyl phosphate. *Wear* 21(2):289–302, 1972.
- Y Ma et al. The effect of oxy-nitrided steel surface on improving the lubricating performance of tricresyl phosphate. *Wear* 210(1–2):287–290, 1997.
- T Morimoto. Effect of phosphate on the wear of silicon nitride sliding against bearing steel. *Wear* 169(2):127–134, 1993.
- B Koch, E Jantzen, V Buck. Properties and mechanism of action of organic phosphoric esters as antiwear additives in aviation. *Proc. 5th Int Tribol Coll.*, Esslingen, Ger., Vol 1, 3/11/1–3/11/12, 1986.
- Y Yamamoto, F Hirano. The effect of the addition of phosphate esters to paraffinic base oils on their lubricating performance under sliding conditions. *Wear* 78(3):285–296, 1982.
- M Kawamura, K Fujito. Organic sulfur and phosphorus compounds as extreme pressure additives. *Wear* 72(1):45–53, 1981.
- Y Garaud, MD Tran. Photoelectron spectroscopy investigation of tricresyl phosphate antiwear action. *Analisis* 9(5):231–235, 1981.
- Y Yamamoto, F Hirano. Effect of different phosphate esters on frictional characteristics. *Tribol Int.* 13(4):165–169, 1980.
- A Riga, WR Pistillo. Surface and solution properties of organophosphorus chemicals and performance relationships in wear tests. *Proc 27th NATAS Ann Conf Therm Anal Appl.* pp. 708–713, 1999.
- A Riga, J Cahoon, WR Pistillo. Organophosphorus chemistry structure and performance relationships in FZG gear tests. *Tribol Lett* 9(3,4):219–225, 2001.
- D Ren, AJ Gelman. Reaction mechanisms in organophosphate vapor phase lubrication of metal surfaces. *Tribol Int* 34(5):353–365, 2001.

2 NEUTRAL PHOSPHITES

- PI Sanin et al. *Tr. Inst. Nefti. Akad. Nauk SSSR*, 14:98, 1960.
- PI Sanin, AV Ul'yanova. *Prisadki Maslam Topliva*, Trudy Naucha. Tekhn. Soveshch., 189, 1960.

- Y Wan, Q Xue. Effect of phosphorus-containing additives on the wear of aluminium in the lubricated aluminium-on-steel contact. *Tribol Lett* 2(1):37–45, 1996.
- GV Barabanova et al. Effect of phosphoric, thiophosphoric and phosphorus acid neutral ester-type additives on the lubricating capacity of C5-C9 synthetic fatty acid pentaerythritol ester. *Pererabotke Nefti* 17:57–61, 1976.
- IM Orudzheva et al. Synthesis and study of some aryl phosphites. 3rd Tekh Konf Neftekhim. 3:411–415, 1974.
- U.S. Patent 3,115,463/4.
- U.S. Patent 3,652,411.
- U.S. Patent 4,374,219.

3 ALKOXYLATED PHOSPHATES

- Xiuling Zhang, Xiaoming Jia. Water soluble phosphate esters. *Hebei Ligong Xueyuan Xuebao* 21(2):58–61, 1999.
- R Wang. Study on water-soluble EP additives. *Runhua Yu Mifeng* 3(17–18):51, 1994.
- X Jia, X Zhang. Antiwear property of water-soluble compound phosphate ester. *Runhua Yu Mifeng* 4(25–25):67, 1999.

4 AMINE SALTS

- Hongxiang Shi. Development trend of phosphorus-nitrogen-type extreme-pressure antiwear agents. *Gaoqiao Shi* 12(3):37–41, 1997.
- ES Forbes et al. The effect of chemical structure on the load carrying properties of amine phosphates. *Wear* 18:269, 1971.

5 DIALKYL ALKYL PHOSPHONATES

- Junjie Tang, Qiuju Cang, Xinhua Zong. Preparation of phosphorus friction modifiers used in automatic transmission fluids. *Shiyu Lianzhi Yu Huagong* 31(3):17–20, 2000.
- Ren-Gen Xiong Wang Hong, Jing-lin Zuo, Cai-Ming Liu, Xiao-Zeng You, Jun-Xiu Dong, Zhang Pei. Antiwear and extreme pressure action of a copper (II) complex with alkyl phosphonic monoalkyl ester. *J Tribol* 118(3):676–680, 1996.
- GTY Wan. The performance of one organic phosphonate additive in rolling contact fatigue. *Wear* 155(2):381–387.
- PME Cann, GJ Johnston, HA Spikes. The formation of thick films by phosphorus-based antiwear additives. *Proc Inst Mech Eng, I. Mech. E. Conf*, pp. 543–554, 1987.
- Y Lozovoi, PI Sanin. Mechanism of action of phosphorus acid esters' type extreme pressure additives. *IZV Khim* 19(1):49–57, 1986.
- AA Gadirov, AK Kyazin-Zade. Diphenyl esters of alpha-aminophosphonic acids as antioxidant and antiwear additives. *Khim Tekhnol Topl Masel* 3:23–24, 1990.
- VL Lashkhi et al. IR spectroscopic study of phosphonic acid esters-antiwear additives for oil. *Khim Tekhnol Topl Masel* 5:59–61, 1977.
- JJ Dickert, CN Rowe. Novel lubrication properties of gold O,O-dialkylphosphorodithioates and metal organophosphonates. *ASLE Trans* 20(2):143–151, 1977.
- VL Lashkhi et al. Antiwear action of organophosphorus and chloroorganophosphorus compounds in lubricating oils. *Khim Tekhnol Topl Masel* 2:47–50, 1975.

6 MIXTURES OF PHOSPHORUS AND SULFUR COMPOUNDS

- Yulin Qiao, Binshi Xu, Shining Ma, Xuejing Fang, Qunji Xue. Study in synergistic effect mechanism of some extreme pressure and antiwear additives in lubricating oil. *Shiyu Xuebao, Shiyu Jiagong* 13(3):33–39, 1997.

- Yulin Qiao, Xuejing Fang, Hongxin Dang. Synergistic effect mechanism of the combination system of two typical additives containing sulfur and phosphorus in lubricating oil. *Mocaxue Xuebao* 15(1):29–38, 1995.
- H Xia. A study of the antiwear behaviour of S-P type gear oil additives in four-ball and Falex machines. *Wear* 112(3–4):335–361, 1986.
- K Kubo, Y Shimakawa, M Kibukawa. Study on the load-carrying mechanism of sulfur-phosphorus type lubricants. *Proc JSLE Int Tribol Conf* 3:661–666, 1985.
- M Kawamura et al. Interaction between sulfur type and phosphorus type EP additives and its effect on lubricating performance. *Junkatsu* 30(9):665–670.

7 GENERAL REFERENCES

- RJ Hartley, AG Papay. Function of additives. Antiwear and extreme pressure additives. *Toraiborojisuto* 40(4):326–331, 1995.
- JM Palacios. The performance of some antiwear additives and interference with other additives. *Lubr Sci* 4(3):201–209, 1992.

Appendix 2 Early Patent Literature on Phosphorus-Containing Compounds

1 NEUTRAL PHOSPHATES

U.S. Patent 2,723,237-Texas Oil Co.

2 NEUTRAL PHOSPHITES

2.1 As AW / EP Additives

British Patent 1 052 751-British Petroleum (chloroethyl phosphite and a chlorparaffin)
British Patent 1 164 565-Mobil Oil Corp. (alkyl or alkenyl phosphite and a fatty acid ester)
British Patent 1 224 060-Esso Research and Engineering Co.
U.S. Patent 2 325 076-Atlantic Refining Co.
U.S. Patent 2 758 091-Shell Development Co. (haloalkyl or haloalkarylphosphites)
U.S. Patent 3 318 810-Gulf Research & Development Co. (phosphites and molybdenum compounds)

2.2 As Antioxidants

U.S. Patent 2 326 140 -Atlantic Refining Co.
U.S. Patent 2 796 400-C.C. Wakefield

3 ACID PHOSPHATES/PHOSPHITES

British Patent 1 105 965-British Petroleum Co Ltd. (acid hydrocarbyl phosphite and phosphates or thiophosphates or phosphoramidates)
British Patent 1 153 161-Nippon Oil Co.
U.S. Patent 2 005 619-E.I. du Pont de Nemours & Co.
U.S. Patent 2 642 722-Tide Water Oil Co.
French Patent 797 449-E.I. du Pont de Nemours & Co.

4 PHOSPHONATES

British Patent 823 008-Esso Research and Engineering Co. (dicarboxylic acid and either a haloalkane phosphonate, a haloalkyl phosphate or phosphite and optionally a neutral alkyl or aryl phosphate)
British Patent 884 697-Shell Research Ltd. (dialkenyl phosphonates)
British Patent 899 101-British Petroleum Co. (amino phosphonates)
British Patent 993 741-Rohm and Haas Co. (aminoalkane phosphonates)
British Patent 1 083 313-British Petroleum Co. (amino phosphonates)
British Patent 1 247541-Mobil Oil Corp. (dialkyl-n-alkylphosphonate or alkylammonium salts of dialkylphosphonates)
U.S. Patent 2 996 452-US Sec of Army (di-(2-ethylhexyl) lauroxyethyl phosphonate)
U.S. Patent 3 329 742-Mobil Oil Corp (diaryl phosphonates)
U.S. Patent 3 600 470-Swift & Co.-(hydroxy or alkoxy phosphonates and their amine salts)
U.S. Patent 3 696 036-Mobil Oil Corp. (tetraoctyl-(dimethylamino) methylene diphosphonate)
U.S. Patent 3 702 824-Texaco Inc. (hydroxyalkylalkane phosphonate)

5 ALKYL- AND ARYLPOLYETHYLENOXY-PHOSPHORUS COMPOUNDS

U.S. Patent 2 372 244-Standard Oil Dev. Co.

6 AMINE SALTS

British Patent 705 308-Bataafsche Petroleum Maatschappij (substituted monobasic phosphonic acid and amine salts thereof)

British Patent 978 354-Shell International Research-(alkali metal-amine salt of a halohydrocarbyl phosphonic acid)

British Patent 1 002 718-Shell International Research (alkyl amine salt of diaryl acid phosphate)

British Patent 1199 015-British Petroleum Co. Ltd. (quaternary ammonium salts of dialkyl phosphates)

British Patent 1 230 045-Esso Research and Engineering Co. (quaternary ammonium salts of alkyl phosphonic and phosphinic acids)

British Patent 1 266 214-Esso Research and Engineering Co. (neutral phosphate and a neutral alkylamine hydrocarbyl phosphate)

British Patent 1 302 894-Castrol Ltd. (tertiary amine phosphonates)

British Patent 1 331 647-Esso Research and Engineering Co. (quaternary ammonium phosphonates)

U.S. Patent 1 936 533-E. I. du Pont de Nemours (triethanolamine salts)

U.S. Patent 3 553 131-Mobil Oil Corp (tertiary amine phosphonate salts)

U.S. Patent 3 668 237-Universal Oil Products Co. (tertiary amine salts of polycarboxylic acid esters of bis(hydroxyalkyl)-phosphinic acid)

7 PHYSICAL MIXTURES OF PHOSPHORUS AND SULFUR AND/OR CHLORINE COMPOUNDS

British Patent 706 566-Bataafsche Petroleum Maatschappij (a phosphorus compound, e.g., a trialkyl phosphate, a glycidyl ether and a disulphide)

British Patent 797 166-Esso Research and Engineering Co. (TCP and a metal soap of a sulphonic acid)

British Patent 841 788-C.C.Wakefield & Co. Ltd. (chlorinated hydrocarbon, a disulphide, and a dialkyl phosphite)

British Patent 967 760-The Distillers Co. Ltd. (disulphides, chlorinated wax, and a haloalkyl ester of an oxy-acid of phosphorus)

British Patent 872 899-Esso Research and Engineering Co. (trialkyl phosphates and chlorinated benzene)

British Patent 1 222 320-Mobil Oil Corp. (diorganophosphonate and a sulphurized hydrocarbon or sulphurized fat)

British Patent 1 287 647-Stauffer Chemical Co. (phosphonates or halogenated alkylphosphates, sulphurised oleic acid, and sebacic acid)

British Patent 1 133 692-Shell International (TCP and triphenylphosphorothionate)

British Patent 1 162 443-Mobil Oil Corp. (neutral or acid, alkyl or alkenyl phosphite, and a sulphurized polyisobutylene, triisobutylene, or a sulphurized dipentene)

U.S. Patent 2 494 332-Standard Oil Dev. Co. (thiophosphates and TCP)

U.S. Patent 2 498 628-Standard Oil Dev. Co. (sulfurized/phosphorised fatty material and TCP or tricresyl phosphite)

U.S. Patent 3 583 915-Mobil Oil Corp (di(organo)phosphonate, and an organic sulphur compound selected from sulphurized oils and fats, a sulphurized monoolefin or an alkyl polysulphide)

8 MISCELLANEOUS PHOSPHORUS COMPOUNDS

British Patent 1 035 984-Shell Research Ltd. (diaryl chloroalkyl phosphate or thiophosphate)

British Patent 1 193 631-Albright & Wilson Ltd. (hydroxyalkyl disphosphonic acid/ alkylene oxide reaction products)

British Patent 1 252 790-Shell International Research (pyrophosphonic and pyrophosphinic acids and their amine salts)

U.S. Patent 3 243 370-Monsanto Co. (phosphinylhydrocarbyloxy phosphorus esters)

U.S. Patent 3 318 811-Shell Oil Co. (diacid diphosphate ester)

U.S. Patent 3 640 857-Dow Chemical Co. (tetrahaloethyl phosphates)

4

Detergents

SYED Q. A. RIZVI

King Industries, Inc. Norwalk, Connecticut, U.S.A.

1 INTRODUCTION

Modern equipment must be lubricated in order to prolong its lifetime. A lubricant* performs a number of critical functions. These include lubrication, cooling, cleaning and suspending, and protecting metal surfaces against corrosive damage [1]. Lubricant comprises a base fluid and an additive package. The primary function of the base fluid is to lubricate and act as a carrier of additives. The function of additives is either to enhance an already-existing property of the base fluid or to add a new property. The examples of already-existing properties include viscosity, viscosity index, pour point, and oxidation resistance. The examples of new properties include cleaning and suspending ability, antiwear performance, and corrosion control. The extent of the desirability of various properties differs from lubricant to lubricant and largely depends on the conditions of use. Automotive use, for example, requires lubricants with good oxidation resistance, suitable low- and high-temperature viscosities, high-viscosity index (i.e., minimum loss in viscosity with an increase in temperature), and good cleaning and suspending ability. Conversely, the use as nonautomotive lubricants, such as industrial and metal-working lubricants, emphasizes oxidation resistance, antiwear performance, corrosion control, and cooling ability.

One of the most critical properties of the automotive lubricants, especially engine oils, is their ability to suspend undesirable products from thermal and oxi-

*The terms “lubricant” and “oil” are interchangeable and are different from the terms “base oil” and “base fluid”. Lubricant and oil imply base oil or a base fluid plus additives.

ductive degradation of the lubricant. Such products form when the byproducts of fuel combustion, such as hydroperoxides and free radicals, go past piston rings into the lubricant and, being reactive species, initiate lubricant oxidation. The resulting oxidation products are thermally labile and decompose to highly polar materials with a tendency to separate from the bulk lubricant and form surface deposits and clog small openings. The former will lead to malfunctioning of the closely fitted surfaces, such as those between pistons and cylinder walls, and the latter will impair oil flow to parts needing lubrication. The separation tendency of these products relates to their high polar–nonpolar ratio [2], which makes them less soluble in largely nonpolar base oil. A lubricant with high-oxidation resistance, due to the quality of the base fluid and/or the presence of a good oxidation inhibitor additive package, will slow down the formation of these undesirables.

Oxidation inhibitors, detergents, and dispersants make up the general class of additives called *stabilizers and deposit control agents*. These additives are designed to control deposit formation, either by inhibiting the oxidative breakdown of the lubricant or by suspending the harmful products already formed in the bulk lubricant. Oxidation inhibitors intercept the oxidation mechanism, and dispersants and detergents perform the suspending part [3, 4]. *Detergents* are the topic of this chapter, and *dispersants* are the topic of the subsequent chapter. Detergents are metal salts of organic acids that frequently contain associated excess base, usually in the form of carbonate. Dispersants are metal-free and are of higher molecular weights than detergents. The two types of additives work in conjunction with each other.

The final products of combustion and lubricant decomposition include organic and inorganic acids, aldehydes, ketones, and other oxygenated materials [4, 5]. The acids have the propensity to attack metal surfaces and cause corrosive wear. Detergents, especially basic detergents, contain reserve base that will neutralize the acids to form salts. While this decreases the corrosive tendency of the acids, the solubility of the salts in the bulk lubricant is still low. The organic portion of the detergent, commonly called “soap”, has the ability to associate with the salts to keep them suspended in the bulk lubricant. However, in this regard, detergents are not as effective as dispersants because of their lower molecular weight. The soap in detergents and the dispersants also have the ability to suspend nonacidic oxygenated products, such as alcohols, aldehydes, and resinous oxygenates [4]. The mechanism by which this occurs is depicted in [Figure 1](#).

Dispersants and detergents together make up the bulk, about 45–50%, of the total volume of the lubricant additives manufactured. This is a consequence of their major use in engine oils, transmission fluids, and tractor hydraulic fluids, all of which are high-volume lubricants [6].

As mentioned, detergents neutralize oxidation-derived acids as well as help suspend polar oxidation products in the bulk lubricant. Because of this, these additives control rust, corrosion, and resinous buildup in the engine. Like most additives detergents contain a surface-active polar functionality and an oleophilic hydrocarbon group, with an appropriate number of carbon atoms to ensure good oil solubility [2]. Sulfonate, phenate, and carboxylate [7] are the common polar groups present in detergent molecules. However, additives containing salicylate and thiophosphonate functional groups are also sometimes used.

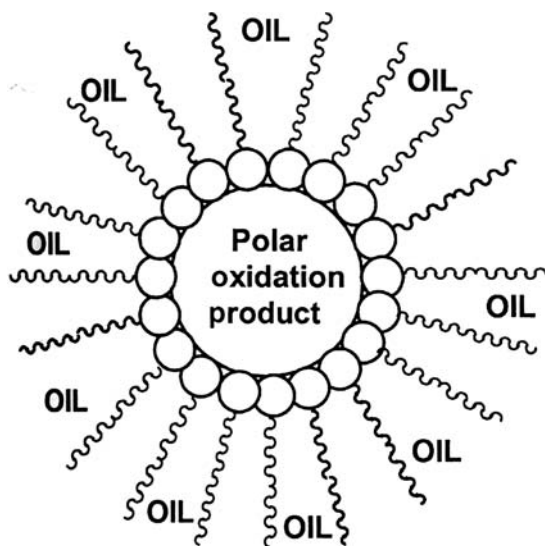


Figure 1 Oil suspension of polar oxidation products.

2 DETERGENT TYPES

Detergents are the metal salts of organic acids. The acids normally used to synthesize these compounds include arylsulfonic acids, such as alkylbenzenesulfonic acids and alkylnaphthalenesulfonic acids [8–11]; alkylphenols [12–16]; carboxylic acids, such as fatty carboxylic acids, naphthenic acids, and petroleum oxidates [17–20]; and alkenylphosphonic and alkenylthiophosphonic acids [21–23]. Sometimes a mixture of different types of acids is also employed [24]. The reaction of these acids with inorganic bases, such as metal oxides, metal hydroxides, and metal carbonates, results in the formation of salts [7]. The quantity of the metal used may be equal to (stoichiometric amount) or in excess of the exact amount necessary to completely neutralize the acid functionality. The presence of metal in stoichiometric amount results in the formation of the neutral salt, often referred to as a neutral detergent or soap. If the metal is present in excess, the detergents are called *basic*, *overbased*, or *superbased* [7, 25]. It is important to note that basic detergents appear as clear homogeneous fluids, the same as neutral detergents, because the excess metal is present in a colloidal form [26]. The general formulas for metal sulfonates, metal phenates, and metal carboxylates are presented in Figure 2.



Basic Sulfonate



Basic Phenate



Basic Carboxylate

a and $c = 1$ and $b = 2$, if the metal M is monovalent; a and $c = 2$ and $b = 1$, if the metal M is divalent.

Figure 2 General formulas for detergents. (From Ref. 6.)

The excess base in basic detergents may be present as metal hydroxide, metal carbonate, or both. For neutral detergents, x and y in the formulas in Figure 2 are zero. For low overbased detergents, such as those with a base number of about 50 or less, x may be zero and y may be a low number, or both x and y may be low numbers. This implies that slightly overbased detergents either are carbonate-free or contain a mixture of both the hydroxide and the carbonate. Highly overbased detergents invariably have a large amount of carbonate as the reserve base. That is, in their case, y is low and x is very high. In some cases, x can be as high as 20, or more. In summary, the excess base per equivalent of acid in metal hydroxide-containing detergents is generally lower than that in metal carbonate-containing detergents.

3 DETERGENT PARAMETERS

Detergents are described chemically in terms of their metal ratio, percent sulfated ash, degree of overbasing or conversion, soap content, and total base number (TBN) [7].

The *metal ratio* is defined as the total equivalents of metal per equivalent of acid. The *percent sulfated ash* is the ash produced when the detergent is treated with sulfuric acid and burned. All organic material in the detergent burns, leaving behind the metal sulfate ash. Sulfate ash results from the reaction of metal compound with sulfuric acid either directly, as with metal hydroxide and metal carbonate, or through the oxidative degradation of the metal sulfonate. Detergents are not the only additives that result in sulfate ash. Other metal-containing additives in the lubricant also contribute toward it. Such additives include metal carboxylates and metal dialkyl dithiophosphates, such as zinc dialkyl dithiophosphate. The former compounds are sometimes used as friction modifiers and corrosion inhibitors, and the latter compounds are commonly used as oxidation inhibitors and antiwear agents. Because the metal compounds can lead to the formation of the inorganic material (ash) on combustion, a formulator must know the metal content of a formulation to offset any problems that might occur. This is because the lubricant travels past piston rings into areas that experience flame and high temperatures, such as the top land and the groove behind the top ring, it burns to produce ash. Ash is undesired because it is believed to initiate deposit formation. Sulfated ash is one of the methods used to assess the metal content of a lubricant; and the methods to determine this are described in the ASTM Standards D 482 and D 874 [27].

The *degree of overbasing* is the number of equivalents of the metal base per equivalent of the acid substrate. This is usually expressed as *conversion*, which indicates the amount of inorganic material relative to that of organic material. Conversion is expressed as the number of equivalents of base per equivalent of acid times 100 [7]. The *soap content* is the amount of the neutral salt as a percent of the detergent composition.

The *total base number*, or *TBN*, of the detergent reflects its ability to neutralize acids. For basic sulfonate and phosphonate detergents, only the overbased portion of the detergent, that is, the carbonate and the hydroxide (see Figure 2), possesses this capability. The neutral metal sulfonates and phosphonates, that is, soaps, lack this ability. However, for basic carboxylates, salicylates, and phenates, the soaps also

possess the acid-neutralizing ability. This is because, unlike sulfonates and phosphonates that are strong acid–strong base salts, metal carboxylates, metal salicylates, and metal phenates are strong base-weak acid salts. This makes them Lewis bases, hence the acid-neutralizing ability.

Let us try to calculate the detergent parameters for a detergent of a hypothetical molecular formula $(\text{RSO}_3)_v\text{Ca}_w(\text{CO}_3)_x(\text{OH})_y$.^{*} In this formula, v , w , x , and y denote the number of sulfonate groups, the number of calcium atoms, the number of carbonate groups, and the number of hydroxyl groups, respectively. The *metal ratio*, the total equivalents of metal per equivalent of acid, for such a detergent equals $2w/v$. The coefficient 2 signifies the divalent nature of calcium. For metals such as sodium and potassium, which are monovalent, the ratio equals w/v . The degree of overbasing or conversion, which is metal ratio times 100, is $(w \times 100)/v$ for monovalent metals and $(2w \times 100)/v$ for divalent metals. Neutral detergents, or soaps, have a conversion of 100 because the ratio of equivalents of base to the equivalents of acid is 1. *Soap content* for such a detergent can be calculated by the following formula:

$$\text{Percent soap} = \frac{\text{formula weight } [\text{RSO}_3]_2\text{Ca} \times 100}{\text{effective formula weight}} \quad (4.1)$$

The effective formula weight is the weight of all the atoms that make up the formula $(\text{RSO}_3)_v\text{Ca}_w(\text{CO}_3)_x(\text{OH})_y$ plus the diluent, if present. The diluent can be the incidental alkylate that does not get sulfonated or the diluent oil that is intentionally added. If one must add oil, most of it is added to reactants at the beginning of the reaction, especially during the manufacture of basic detergents. The presence of diluent is believed to facilitate micelle formation, thereby making the process more efficient. Adding oil after the reaction is not as effective.

The total base number, or *TBN*, indicates a detergent's ability to neutralize acids. In additives and formulated lubricants the *TBN* is expressed as mg KOH/g of additive [27]. The method to determine base numbers is described in the ASTM Standard D 974 [28]. For sulfonate and phosphonate detergents, it can be calculated by using the number of equivalents of excess metal after salting the acid, that is $(2w - v)$, according to the following equation.

$$\text{TBN (mg KOH/g)} = \frac{(2w - v) \times 56,100}{\text{effective formula weight}} \quad (4.2)$$

To calculate the base number of monovalent metal-derived sulfonates, one must use only $(w - v)$ in the above equation. For divalent metal-derived carboxylate, salicylate, and phenate detergents, the equation to be used is.

$$\text{TBN (mg KOH/g)} = \frac{(2w) \times 56,100}{\text{effective formula weight}} \quad (4.3)$$

For monovalent metal salt of this type, the numerator will be $w \times 56,100$. As mentioned earlier, the *percent sulfated ash* is the quantity of solid metal sulfate that results when the detergent is treated with sulfuric acid and the mixture ignited. Theoretical sulfated ash for divalent and monovalent metals can be calculated using

^{*}The correct formula for such a detergent is $(\text{RSO}_3)\text{Ca}_x\text{CaCO}_3.y\text{Ca}(\text{OH})_2$.

the following equations. Equation (4) is for divalent metals, and Eq. (5) is for monovalent metals.

$$\text{Percent sulfated ash} = \frac{w \times \text{molecular weight of } \text{M}_2\text{SO}_4 \times 100}{\text{atomic weight of metal M} \times \text{effective formula weight}} \quad (4.4)$$

$$\text{Percent sulfated ash} = \frac{0.5w \times \text{molecular weight of } \text{M}_2\text{SO}_4 \times 100}{\text{atomic weight of metal M} \times \text{effective formula weight}} \quad (4.5)$$

4 DETERGENT SUBSTRATES

A variety of organic acids is used to synthesize detergents. These include alkylaromatic sulfonic acids, alkylphenols, alkylsalicylic acids, fatty carboxylic acids, and alkenylphosphonic acids. Alkylaromatic sulfonic acids, such as alkylbenzenesulfonic acids and alkylnaphthalenesulfonic acids, are made by reacting the respective alkylbenzenes and alkylnaphthalenes with a sulfonating agent. The alkylaromatic starting materials are made via alkylation of aromatics, benzene and naphthalene [29–33]. To make *synthetic* sulfonates, benzene or naphthalene is first alkylated and then sulfonated. The alkylating agent is either an alkyl halide or an olefin. The olefins can be α -olefins, internal olefins, or olefin oligomers, such as polypropylene and polyisobutylene. An acid catalyst is usually required. One may choose from many acids. These include mineral acids, such as sulfuric acid and phosphoric acid; Lewis acids, such as aluminum chloride and boron trifluoride; organic acids, such as methanesulfonic acid; and mixtures thereof [32, 33]. Some of the inorganic acids, such as sulfuric acid, are also available on a solid support, such as Fuller's earth or silica. Unlike other catalysts that require neutralization at the end of the reaction, these catalysts just require filtration to remove them. Zeolites and related mixed-metal oxides also enjoy the same advantage as the solid alkylation catalysts [30, 31]. Another class of catalysts, exemplified by Amberlysts®, is aromatic polymer-derived sulfonic acids [31, 34]. While they have the advantages of being insoluble, hence easier to remove, and of multiple use, they have the disadvantage of being expensive. It is important to note that not all catalysts have equal effectiveness in all alkylations.

Alkylaromatic sulfonic acids are derived either from the sulfonation of alkylaromatics, such as alkylbenzenes and alkylnaphthalenes, or from petroleum refining. The alkylbenzenes and alkylnaphthalenes are converted into respective sulfonic acids by reacting them with a sulfonating agent. The acids thus obtained are called *synthetic* sulfonic acids. Alkylbenzenesulfonic acids are also available from petroleum refining. These are referred to as *natural* sulfonic acids. Detergents made from *synthetic* sulfonic acids are called *synthetic* sulfonates and those made from *natural* sulfonic acids are called *natural* or *petroleum* sulfonates.

The steps involved in making *synthetic* sulfonic acids are shown in Figure 3. The degree of branching in alkylbenzenes and alkylnaphthalenes, commonly called the *alkylate*, increases as we go from α -olefins to internal olefins to olefin oligomers. More branching of the alkylate implies somewhat less efficient sulfonation but better oil solubility of the final sulfonate detergent. The common reagents used to sulfonate

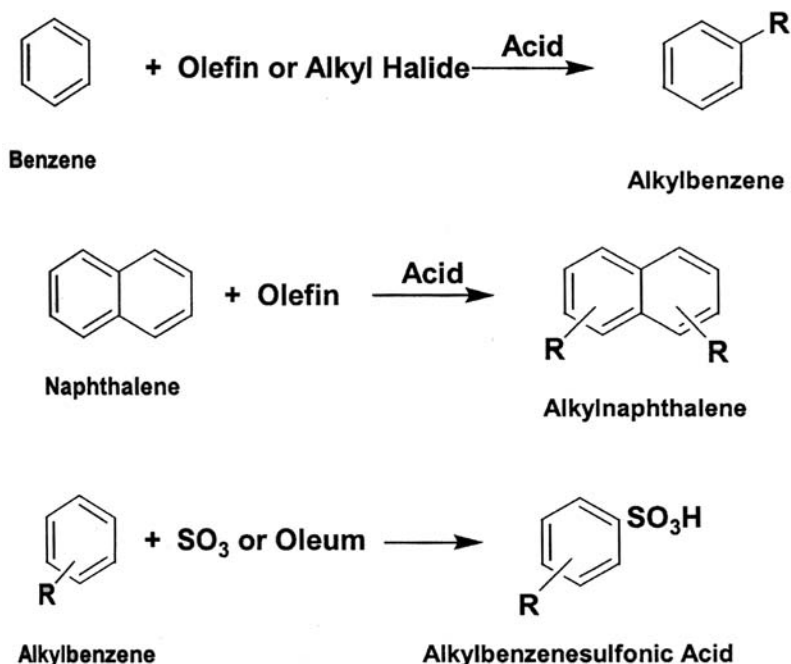


Figure 3 Synthesis of sulfonic acid substrates.

alkylaromatics are sulfur trioxide, fuming sulfuric acid or oleum, and chlorosulfonic acid [35]. Oleum is 15–30% sulfur trioxide dissolved in concentrated sulfuric acid. In general, the alkylate is dissolved in a hydrocarbon solvent, such as hexane or heptane, and reacted with the sulfonating reagent. One obtains a mixture of a monosulfonic acid and di- or higher sulfonic acids. The latter must be removed because of the high polarity of their metal salts, hence potentially lower oil solubility. This can be easily achieved by water washing. The di- and higher sulfonic acids are also undesired because, when reacted with polyvalent metals, they have the tendency to make polymeric salts that are usually of low lubricant solubility as well.

Not all components of the alkylate are sulfonatable. In the case of alkylbenzenes, the species that do not sulfonate easily include polyalkylated benzenes, such as trialkylbenzene, or highly branched dialkylbenzenes. Their sulfonation difficulty is primarily a consequence of the steric crowding of the sulfonatable positions. Mono-alkylbenzenes do not suffer from this drawback and hence sulfonate easily. In general, the sulfonation of branched alkylbenzenes is slower than linear alkylbenzenes. In the case of alkylbenzenes, [Figure 4](#) shows structures that are sulfonatable and those that are not.

With naphthalene, however, steric factors are not as important because of its bicyclic nature. The alkyl groups are likely to be attached to different aryl rings, except for very highly alkylated naphthalenes. Commercial NA-SUL® products are based on alkylnaphthalene chemistry.

During petroleum refining, crude mineral oil is washed with a sulfonating agent, such as sulfur trioxide or oleum [36]. Crude mineral oil contains reactive unsaturated compounds containing multiple bonds and alkylaromatics. These react with

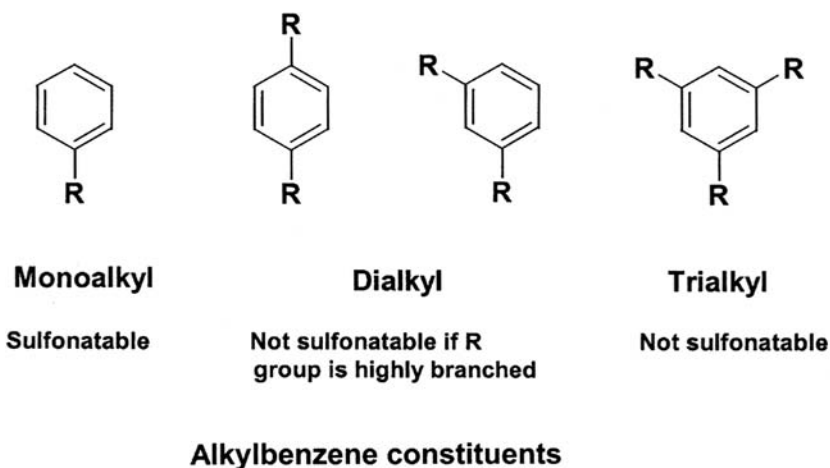


Figure 4 Alkylbenzene structures.

sulfur trioxide to form sulfonic acids. This is a desirable step because oils containing unsaturates and aromatics have a greater susceptibility toward oxidative breakdown, which could lead to the formation of increased deposits. If this occurs, it is likely to lead to equipment malfunction [5, 23, 37–41]. An analogous process is used to manufacture medicinal-quality white oil from petroleum. In the subsequent reaction, the sulfonic acid fraction is reacted with sodium hydroxide to convert the acids into sodium salts. These salts are washed with water to extract *green acid* soaps, which are used in many consumer products. The residual water-insoluble material is then extracted with alcohol. This results in the isolation of *mahogany acid* soaps, which are useful in making detergent additives. The process is summarized in Figure 5.

Alkylphenols are made in a manner analogous to alkylbenzenes, that is, by alkylating phenol with an olefin in the presence of an acid catalyst. The preferred catalysts are sulfuric acid, aluminum chloride, and boron trifluoride [39–41]. The alkylphenols can be either converted directly into their neutral or basic salts or further reacted with sulfur or sulfur dichloride to form sulfur-bridged alkylphenols and with formaldehyde to form methylene-bridged alkylphenols. This is shown in Figure 6.

Alkylsalicylic acids are prepared from alkylphenols by reacting the alkali metal, especially potassium, phenates with carbon dioxide. The reaction is known as the Kolbe–Schmitt reaction [42]. Like the *natural* sulfonate process, this process yields alkali metal salts.

These must be either neutralized with a mineral acid to free acids in order to use them to make detergents or reacted directly with a metal halide, such as calcium chloride or magnesium chloride, to make the calcium or magnesium soaps [43].

Alkenylphosphonic and alkenylthiophosphonic acid detergents are only rarely used. The acids are prepared by reacting polyisobutylene of varying molecular weights with phosphorus pentasulfide and the subsequent hydrolysis of the resulting adduct [44, 45]. The adduct is believed to result from an ene-type addition of phosphorus pentasulfide to polyolefin. This type of addition does not result in the loss of the double bond, but it shifts the double bond down the carbon chain. Unless steric factors hinder the reaction, at least theoretically, the ene product can react with

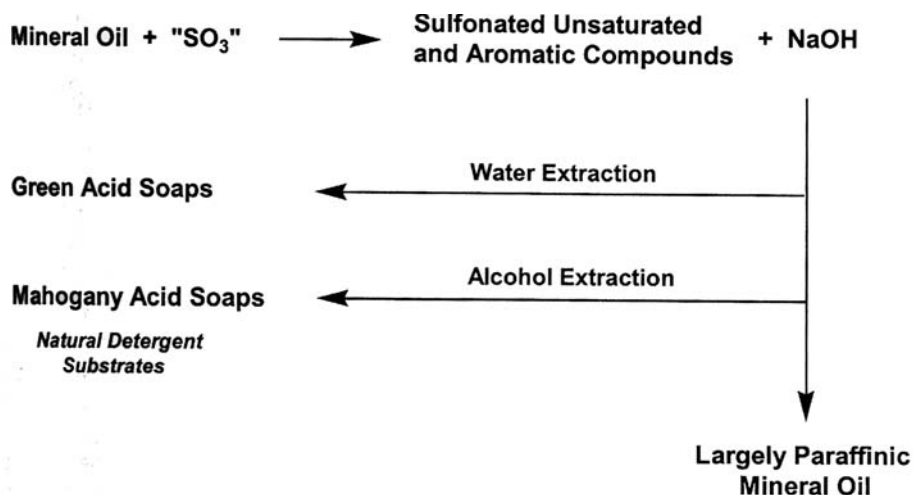


Figure 5 Isolation of *natural* sodium sulfonates.

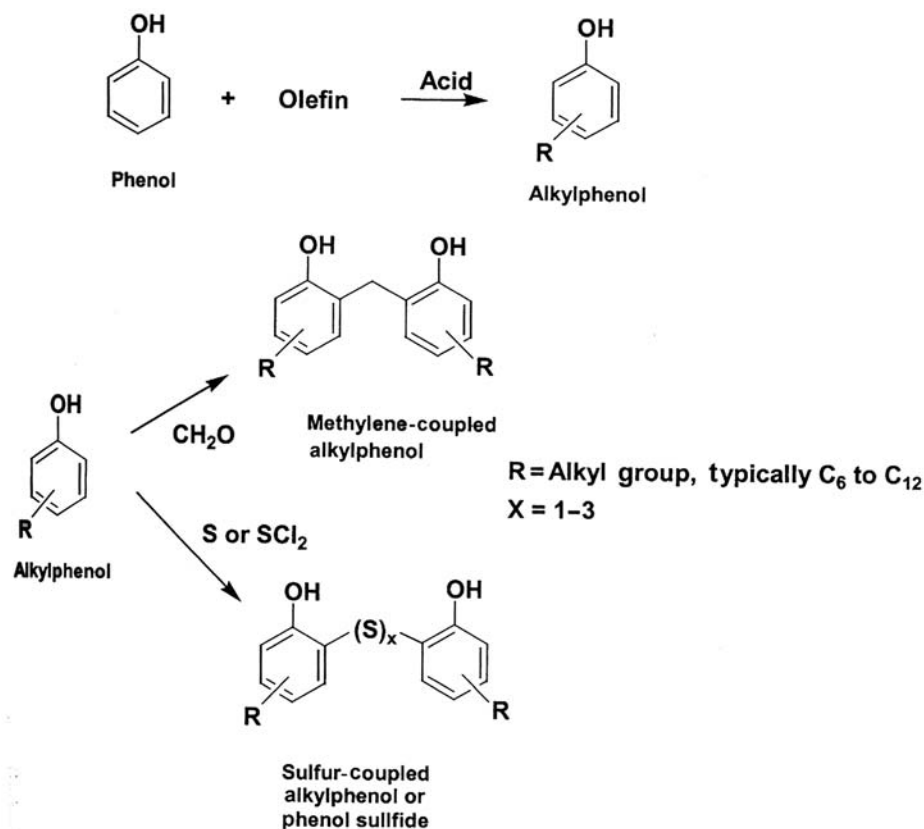


Figure 6 Synthesis of alkylphenol substrates.

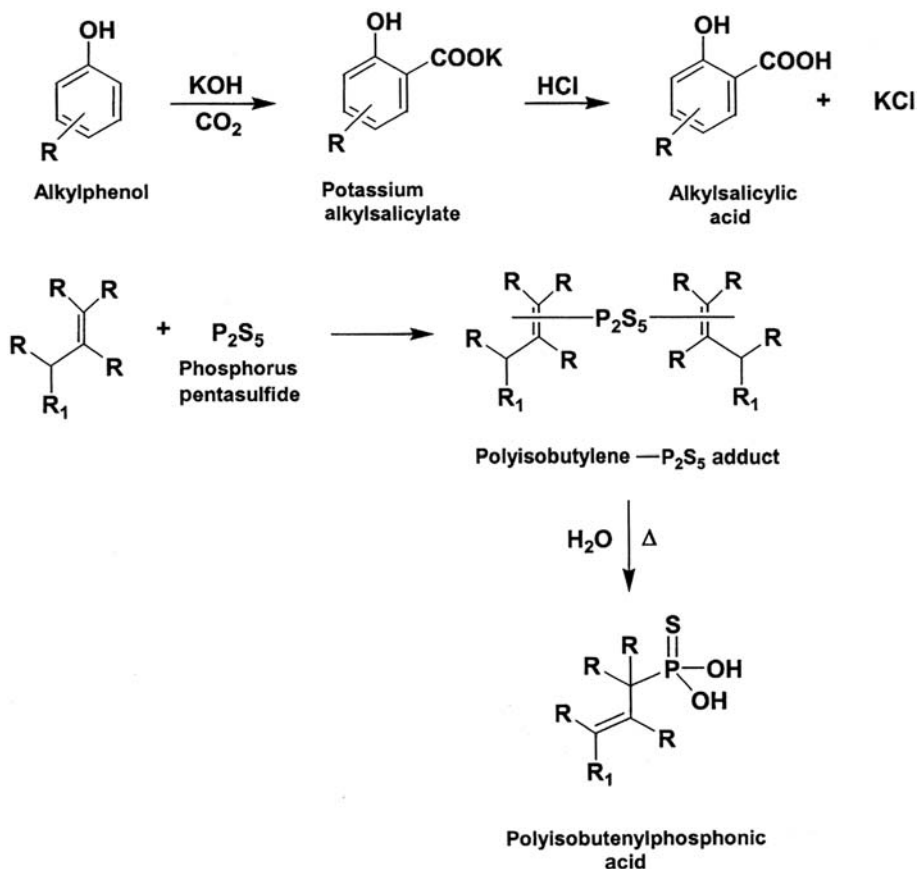


Figure 7 Synthesis of alkylsalicylic acids and alkenylphosphonic acids.

another molecule of phosphorus pentasulfide. This process can extend further. The adduct is hydrolyzed by the use of steam. One obtains a complex mixture of acids that include fully hydrolyzed (sulfur-free) alkenylphosphonic acids and partially hydrolyzed (contain residual sulfur) alkenylthiophosphonic acids. The reaction schemes to synthesize alkylsalicylic acids and alkenylphosphonic and thiophosphonic acids are shown in Figure 7.

Recently, the development of basic detergents that are not derived from organic acids have been reported [46, 47]. Substrates that can be overbased include organic amines and polyamines, ethers, and organic sulfides (sulfurized olefins). Only alkali metal-derived overbased materials have been reported.

5 NEUTRAL AND BASIC DETERGENT SYNTHESIS

In order to make detergents, the organic acids are reacted with a metal base, such as a metal oxide or a metal hydroxide. In general, the reaction between the organic acid and the inorganic base is not good because of poor contact between the two reactants. A number of compounds, called *promoters*, are used to facilitate salt

formation and the subsequent carbonation or a related reaction. Common promoters include ammonium hydroxide, low molecular weight carboxylic acids, such as formic acid and acetic acid, low molecular weight alkylphenols, and other polar compounds, such as nitroalkanes and imidazolines. A comprehensive list of such agents is provided elsewhere [49]. Most of these reagents are used in combination with water, except for high-temperature overbasing reactions where water will not stay in. In such cases, alcohols, such as 2-ethylhexanol or iso-octyl alcohol, and alkylphenols that have high boiling points are used. When water is present as part of the promoter system, it either is added or results from the neutralization reaction. The promoters are surfactants, that is, they contain a hydrophilic moiety, such as a hydroxyl group or a carboxylic acid functionality, and a reasonably sized alkyl group to impart somewhat of a hydrophobic character to the molecule.

Not all promoters are effective for all overbasing reactions, and one has to experiment to select the right promoter system. For low-temperature overbasing ($\leq 100^{\circ}\text{C}$), alcohol–water mixtures are commonly used, for high-temperature overbasing ($\geq 100^{\circ}\text{C}$), low molecular weight alkylphenols are used. The structure of the final detergent from the two processes is believed to be different and hence the performance in certain tests. The role of promoters in the overbasing reaction is not well understood. One explanation regarding their role is based on their preferential reaction with the base to form an alkoxide or a phenoxide. This species then transfers the metal to the substrate, thereby facilitating salt formation and/or overbasing. The other explanation is based on their acting as a surfactant and a wetting agent. This improves contact between the base and the substrate, thereby assisting the reaction to occur. The second explanation is definitely more plausible than the first. However, in high-temperature overbasing reactions, usually carried out under anhydrous conditions, the first explanation may have merit.

While a number of metals can be used to make neutral salts (soaps), fewer metals have the ability to result in oil-soluble basic detergents. The common metals that can be used for this purpose include lithium, sodium, and potassium in Group I and magnesium, calcium, strontium, and barium in Group II of the periodic table. Aluminum is the only overbasable metal in Group III. Overbased salts of transition metals, such as zinc, copper, cadmium, molybdenum, copper, manganese, cobalt, nickel and iron, from sulfonic acids, alkylphenols, and naphthenic acids are also reported in the patent literature [19, 51, 52]. The ability to overbase relates to a metal's, base strength: the higher the basic character, the easier it is to overbase. For Group I metals, where basic character increases from lithium to sodium to potassium, it is easier to overbase potassium than it is to overbase lithium. In Group II metals, the basic character increases from magnesium to calcium to strontium to barium; hence it is easier to overbase barium than it is to overbase magnesium.

A variety of detergents derived from metal anions other than hydroxide and carbonate is reported in the patent literature. The anions include sulfites, sulfates, thiosulfates, borates, and phosphates [32, 48–50, 53, 54]. These detergents are obtained either from the carbonate detergent by displacing the carbonate anion with the alternative anion, or by using the anion precursor during overbasing. For example, one can obtain metal sulfite overbased detergent either by blowing sulfur dioxide during overbasing or by displacing carbon dioxide in a carbonate detergent with sulfur dioxide. The resulting metal sulfite detergent can be oxidized to a sulfate

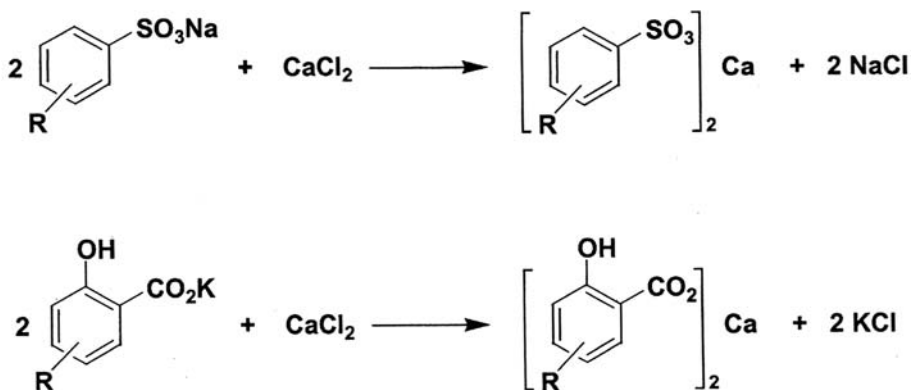


Figure 8 Double-decomposition reaction.

detergent by using an oxygen source, such as oxygen gas or a peroxide, or to a thio-sulfate detergent by reacting it with elemental sulfur [48–50]. The borate and phosphate overbased compositions can be made using boric acid or phosphoric acid during the reaction [53, 54].

Common commercial detergents are derived from calcium, magnesium, sodium, and barium. The metals are listed in order of preference. As mentioned, neutral detergents are made by reacting the acid substrate with a stoichiometric amount of the metal base, and overbased detergents are made by reacting the substrate with an excess amount of base in the presence of carbon dioxide. In order to make calcium and magnesium salts from *natural* sulfonic acids and alkylsalicylic acids, one must convert commercially available alkali metal (sodium and potassium) salts (See Figures 5 and 7) into free acids by reacting them with a mineral acid and then reacting the acids with magnesium oxide or calcium hydroxide. Alternatively, alkali metal salts can be converted directly into magnesium and calcium salts via a double decomposition reaction with a metal halide, as shown in Figure 8. In order to make the *natural* sulfonate detergent, one must react the mahogany acid soap with a metal halide, such as calcium chloride. The reaction converts the sodium sulfonate soap into calcium sulfonate, which can be overbased if desired. Because of the extensive branching, *petroleum*-derived sulfonates have better oil solubility than *synthetic* sulfonates of similar molecular weight. Figure 9 presents the idealized structures for neutral detergents.

In order to make overbased detergents, one can use either a two-step process or a one-step process. Generally, the one-step process is preferred over the two-step process. In the two-step process, the neutral salt or the soap is made first, which is subsequently overbased. In the one-step process, the excess metal base is charged to the reaction; once the neutral salt formation is complete, carbon dioxide blowing (carbonation) of the reaction is initiated. When carbon dioxide uptake stops, the reaction is considered complete and it is worked up to isolate the product. Figure 10 summarizes the two processes. For making overbased natural sulfonates and alkylsalicylates, one can double-decompose alkali metal salts in situ by reacting with a metal halide and overbasing. The alkali metal halide byproduct need not be removed until the overbasing is complete. It comes out during the final filtration,

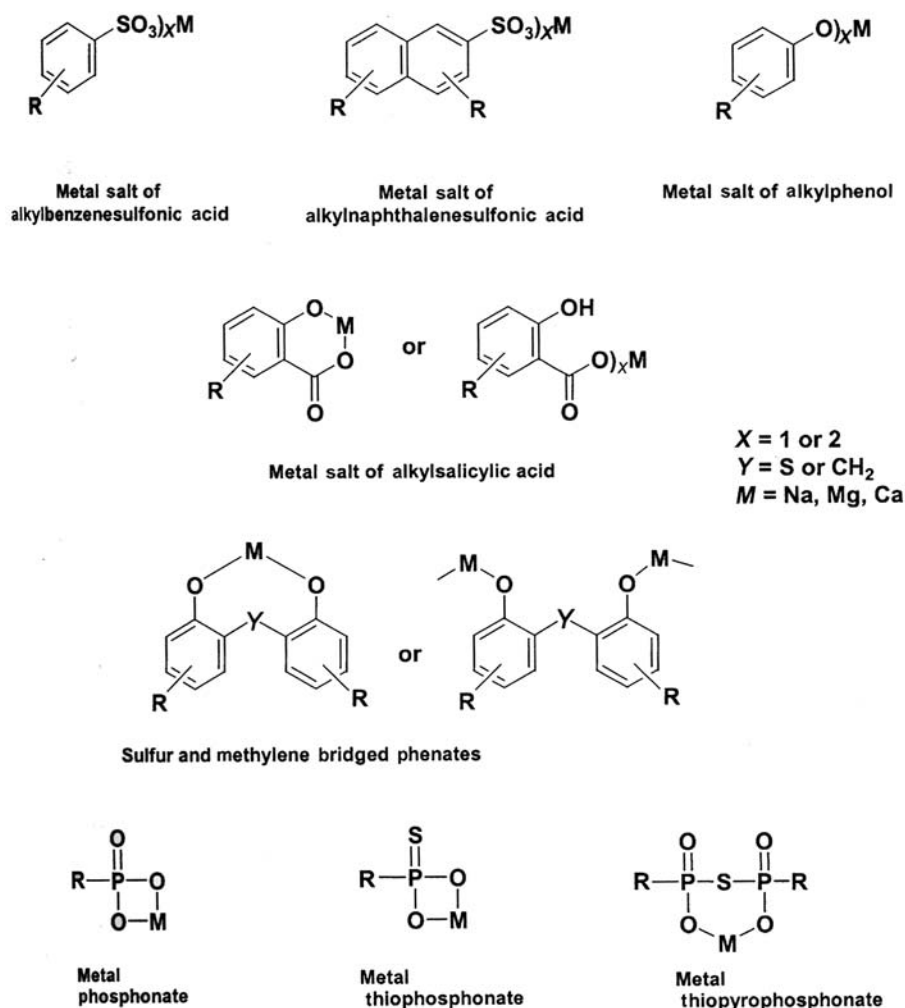
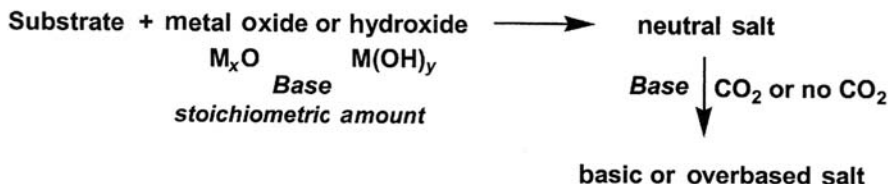
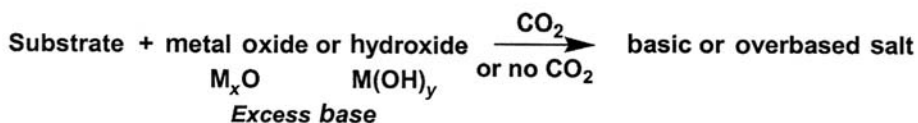


Figure 9 Idealized structures of neutral salts (soaps).

which is employed to remove any unreacted excess base and other particulate materials.

As mentioned, common metals that can be used to make neutral or basic detergents include sodium, potassium, magnesium, calcium, and barium. Calcium and magnesium find most extensive use as lubricant additives, with a preference for calcium due to its lower cost. The use of barium-derived detergents is being curbed due to concerns for barium's toxicity. Technically, one can use metal oxides, hydroxides, and carbonates to manufacture neutral (non-overbased) detergents; for non-overbased detergents, oxides and hydroxides are the preferred bases. For sodium, calcium, and barium detergents, sodium hydroxide, calcium hydroxide, and barium hydroxide are often used. For magnesium detergents, however, magnesium oxide is the preferred base.

Two-step process:**One-step process:**

Basic salts = neutral salts · M_xO, M(OH)_y, or M_xCO₃

M = Na, Mg, Ca, or Ba

x = 1 and y = 2 for Mg, Ca, and Ba (divalent metals)

x = 2 and y = 1 for Na (monovalent metal)

Figure 10 Processes to make basic detergents.

During the synthesis of calcium detergents, overbasing is usually stopped before all the metal base is converted into calcium carbonate. As a result, the excess base is present as a mixture of calcium hydroxide and calcium carbonate. The calcium carbonate predominates because, if the reaction is overblown with carbon dioxide, the amorphous calcium carbonate, which is desired, is converted into crystalline calcium carbonate. Of low solubility in the overbased system, crystalline calcium carbonate falls out of solution, and one obtains an oil-insoluble gellike product. While such products are of little use as lubricant additives, they are useful as rheology control agents in coatings. The challenge is to make them on a consistent basis. Lubrizol supplies such products derived from alkylbenzenesulfonic acids as its Ircogel® product line. Gelled carboxylates and solid calcium micellar complexes have also been reported in the patent literature [55–57].

Basic detergents contain reserve base, which is entrained into the detergent in a colloidal form. The base, such as the carbonate, is believed to be encapsulated by soap molecules. In this arrangement, the polar head group (sulfonate, phenate, or carboxylate) of the soap associates with the carbonate, and the hydrocarbon portion of the soap associates with the oil (see Figure 11). The base neutralizes acids that result from oxidation of the fuel and the lubricant and from the oxidation and thermal decomposition of thermally labile additives.

Some detergents are marketed as neutral or non-overbased. However, most of them have a small amount of reserve base present. In other words, they are overbased to some degree. This implies that no effort was made to overbase them and their reserve base is due to the presence of the unreacted base used to make them.

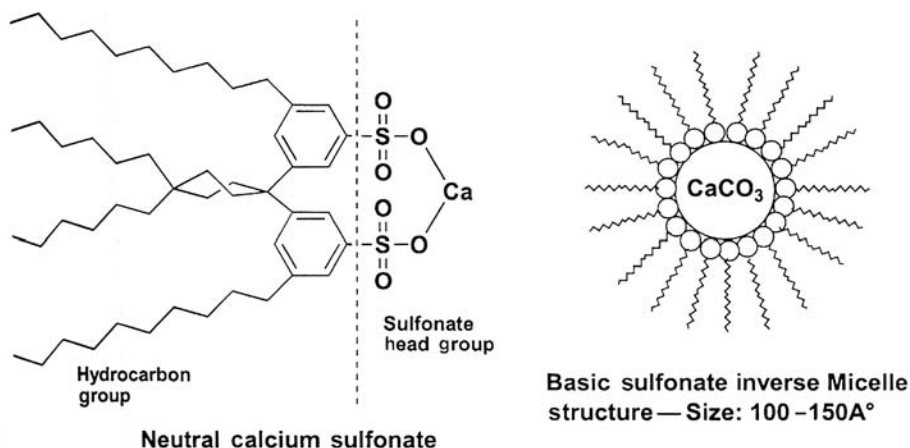


Figure 11 Micelle structure of detergents.

For example, commercially available neutral sulfonates have a TBN of 30 or less, and the base is commonly present as a hydroxide, such as calcium hydroxide. Conversely, “basic” or overbased detergents have a much higher base number, that is, they typically have a TBN of 200 to 500, and the base is commonly present as a metal carbonate.

Calcium-based phenate detergents are easier to make than magnesium-based detergents because alkylphenols are weak acids and their reaction with magnesium oxide, a weak base, is not facile. In order to make the neutral salt, one must react the alkylphenol with a strong base, such as magnesium alkoxide. This reagent can be prepared by reacting magnesium metal with an excess of highly reactive alcohol, such as methanol. However, this method is hazardous because of the hydrogen gas byproduct and costly because of the price of the magnesium metal. Once the neutral salt or soap formation occurs, the excess alcohol is exchanged for an inert solvent, such as toluene or mineral oil, prior to overbasing. Alternatively, one can use a high-temperature overbasing procedure using a low-molecular alkylphenol as a promoter [58]. In the case of methylene or sulfur-bridged phenols that are more acidic than regular alkylphenols, the reactivity toward magnesium oxide is not a problem. And these compounds form neutral and overbased magnesium salts without difficulty. Neutral and basic calcium phenates from alkylphenols, bridged or unbridged, are easy to make because calcium hydroxide, being a stronger base, reacts with them readily. Other acids, that is, alkylsalicylic acids, fatty carboxylic acids, and alkenylphosphonic acids, react with calcium and magnesium bases without any problems.

The synthetic sequences used to make common types of neutral and carbonate overbased detergents are outlined in [Figures 12 to 17](#). Sulfonate, salicylate, and carboxylate detergents are commercially available as calcium and magnesium salts, and phosphonates are available as calcium salts. Some specialty sulfonates, for example NA-SUL BSB®, are also available as barium salts. Phenate detergents are commonly available as calcium salts, and phosphonate detergents are available as both calcium and barium salts. Basic calcium sulfonates make up ~65% of the total detergent market, followed by phenates at ~31%.

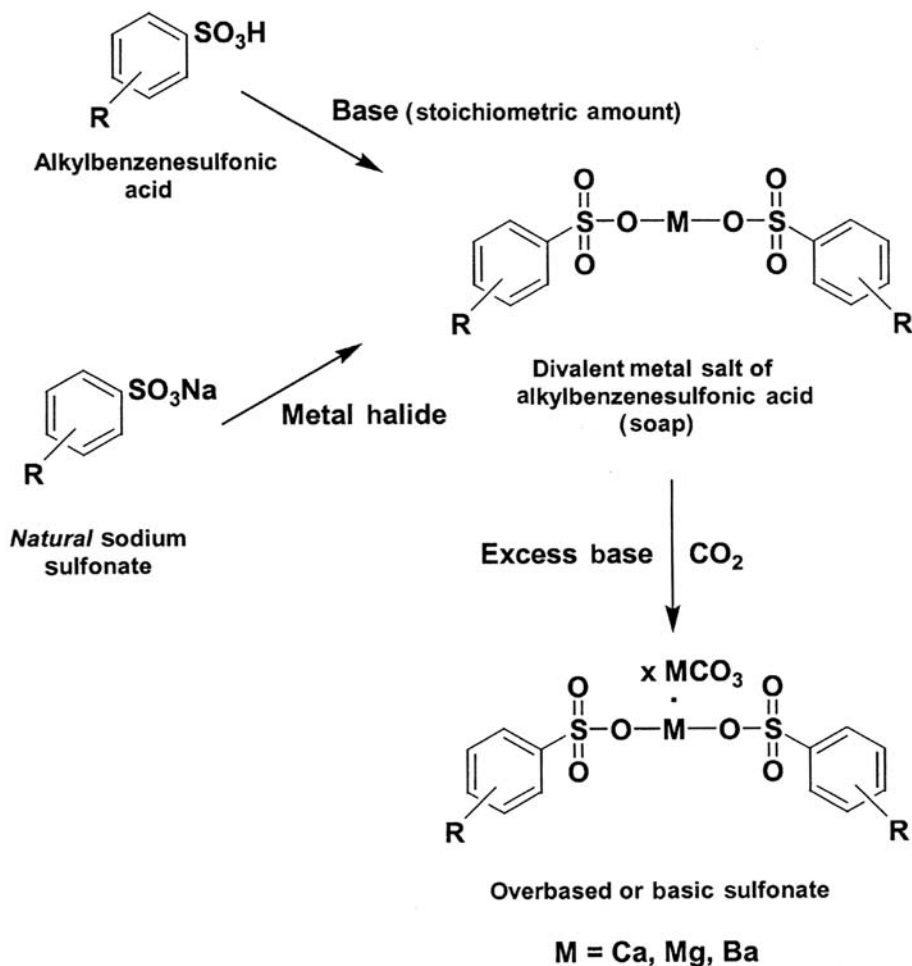


Figure 12 Synthesis of neutral and basic metal sulfonates.

6 TESTING

Detergents are used in engine lubricant formulations to perform two key functions. One is to neutralize the acidic byproducts of lubricant oxidation and thermal decomposition, and the other is to suspend neutral but highly polar oxygenated species in the bulk lubricant.

All components of a lubricant—base oil, additives, and viscosity modifier—oxidize because of their organic nature. Oxidation of the API Group I base oils is more facile than that of the Group II and Group III base oils, primarily because of the presence of aromatic and sometimes olefinic components. These compounds oxidize to form hydroperoxides and radicals [6]. These species are highly reactive and start the oxidation chain reaction. The result is the oxidative breakdown of all components of the lubricant to highly oxygenated polar species, which are of low lubricant solubility. Because of this, these materials, both acidic and neutral, tend to separate on surfaces, thereby impairing the proper functioning of the various

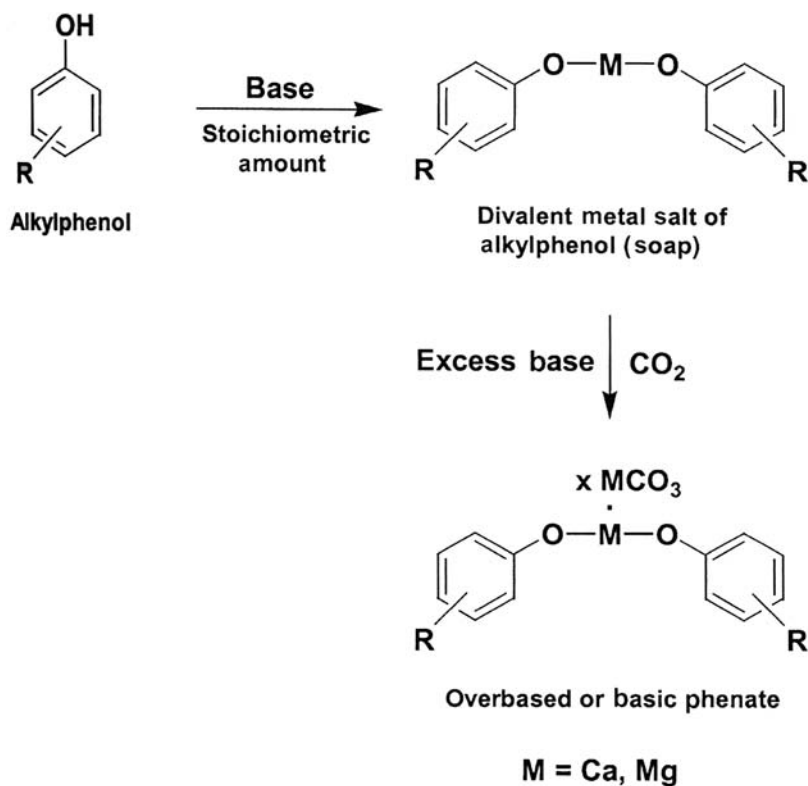


Figure 13 Synthesis of neutral and basic metal phenates.

equipment parts. The acidic materials, such as sulfur oxides, and organic acids resulting from lubricant oxidation can attack metal surfaces and cause corrosion. Sulfur oxides and sulfuric acid result from the combustion of fuel sulfur or the oxidation of sulfur-containing additives, such as sulfurized olefins or zinc dialkyl dithiophosphates. The function of the detergent in this case is to neutralize these acids, hence contain corrosion. The reserve base in detergents primarily performs this function. The soap portion keeps oil-insoluble polar products suspended in oil.

Phenates, sulfurized phenates, and salicylates can also act as oxidation inhibitors because of the presence of the phenol functionality. Phenols are well known for their oxidation-inhibiting action [5]. Detergents are also effective corrosion inhibitors, especially basic detergents [25, 26], because they not only neutralize corrosive acidic products but also form surface films that isolate metal surfaces from corrosive agents [6]. The carbonate portion in the detergent performs acid neutralization, and the soap portion forms the protective surface film. NA-SUL 729® and NA-SUL CA-50® are examples of commercial corrosion inhibitors belonging to this class of additives. The tests that evaluate rust and corrosion are described elsewhere [6, 59]. Detergents derived from fatty carboxylic acids are good friction modifiers, primarily because of the linear structure of their soaps [6].

Detergents find primary use in engine oils, which are responsible for over 75% of the total consumption. The detergent level in marine diesel engine oils is the high-

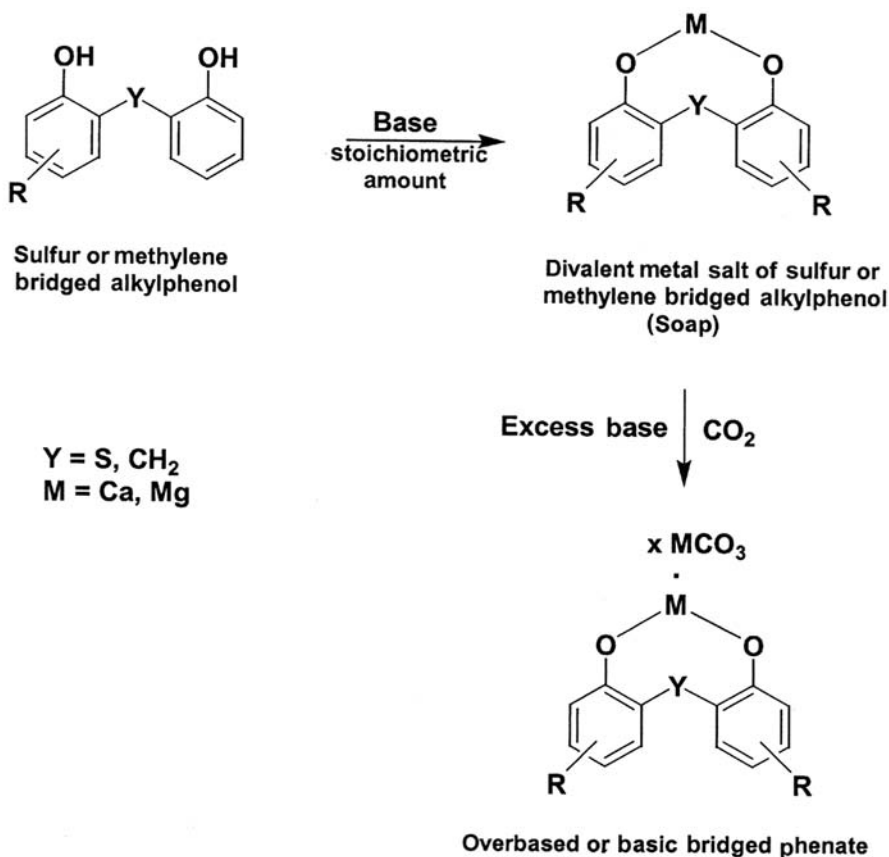


Figure 14 Synthesis of neutral and basic bridged metal phenates.

est because marine engines use high-sulfur fuel, which leads to highly acidic combustion products such as sulfuric acid. The lubricants for these engines therefore require the base reserve of highly overbased detergents.

A variety of proprietary and industry-established tests is used to determine a detergent's effectiveness in lubricants. For gasoline engine oils to be used in North America, these include the CRC L-38, TEOST (Thermo-Oxidation Engine Oil Simulation Test [60]), ASTM Sequence IIIE/IIIF, and ASTM Sequence VE/VG tests. For European gasoline engines, in addition to performance in the ASTM Sequence IIIE/IIIF and VE/VG Engine tests, performance in Peugeot TU3M High-Temperature Test and MB M111 Black Sludge Test is also required. These tests are part of the ACEA 2002 Standard. The standard also includes a sulfated ash limit, which directly affects the amount of detergent used in formulations since it is the primary contributor to sulfated ash.

The efficacy of diesel engine oils for North American use is evaluated by the use of both the single-cylinder and the multicylinder engine tests. Single-cylinder tests include CRC L-38 and Caterpillar 1K, 1M-PC, 1N, 1P, and IR engine tests. CRC L-38's viscosity requirement, an imprecise measure of a detergent's effective-

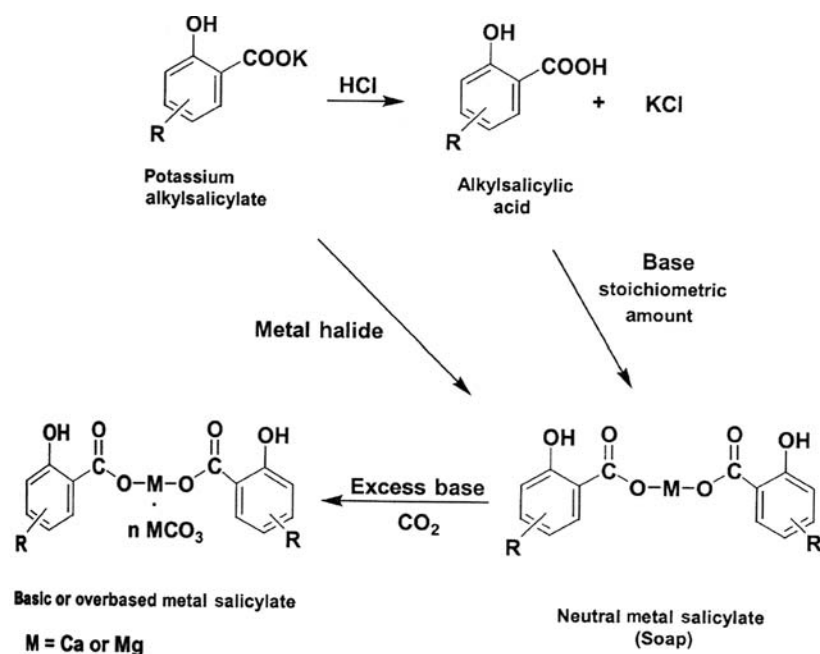


Figure 15 Synthesis of neutral and basic metal salicylates.

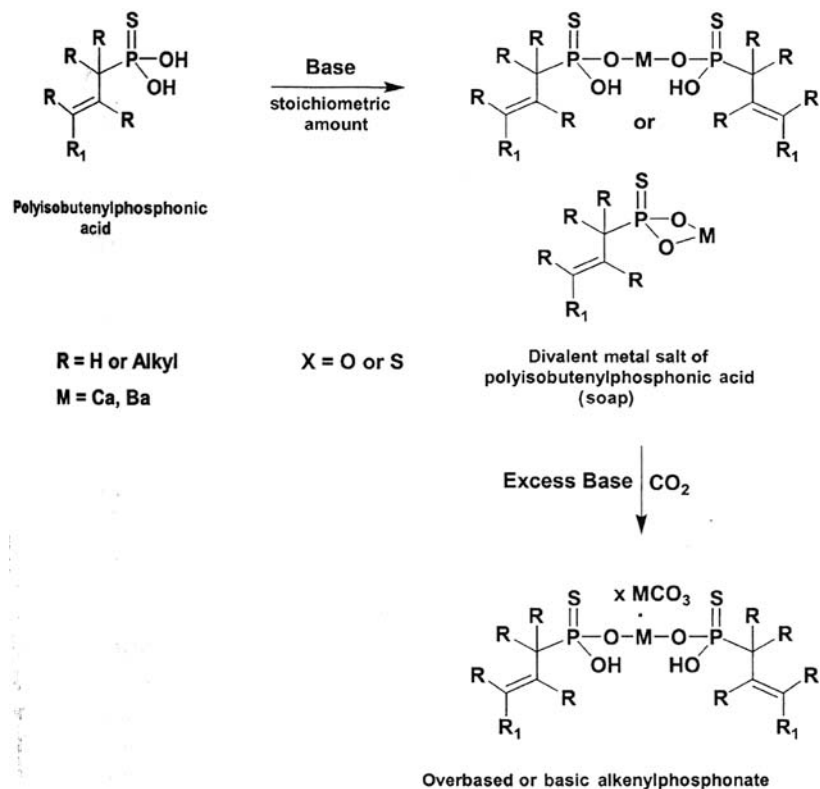


Figure 16 Synthesis of neutral and basic phosphonates.

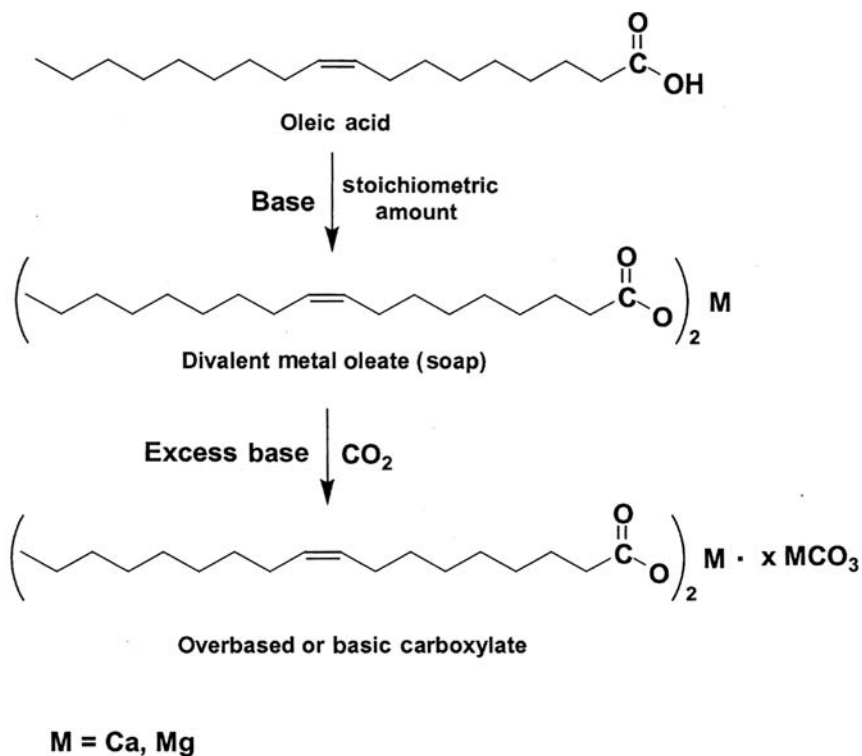


Figure 17 Synthesis of neutral and basic fatty carboxylates.

ness, is a part of the API CG-4 standard. Caterpillar 1K test is a part of the API CF-4, API CH-4, and API CI-4 standards. Caterpillar 1M-PC is a part of the API CF, CF-2, and the U.S. Military's MIL-PRF-2104G specifications. Caterpillar 1N is a part of the API CG-4, API CI-4, and the U.S. Military's MIL-PRF-2104G specifications. Caterpillar 1P is a part of the API CH-4 specification, and caterpillar 1R is a part of the API CI-4 specification. The pass ratings for these tests require meeting the overall appearance of the cylinder and its parts, which is expressed in terms of weighted demerits, percent top groove fill, ring side clearance loss, top land heavy carbon, oil consumption, and stuck rings. All these parameters are related to deposits on the piston and its parts. The multicylinder tests that determine the effectiveness of a detergent include Detroit Diesel 6V92TA engine test (a part of the API CF-2 and MIL-PRF-2104G specifications) and Mack M11 engine test, which is a part of the API CH-4 and CI-4 specifications. These two tests evaluated a detergent's ability to prevent deposit-related port plugging and engine sludge, respectively for European use, oils must pass the requirements of tests, such as VW1.6L TC diesel, XUD11BTE, VWDI, MB OM 364 LA, and MB OM 441LA. These tests evaluate ring sticking, piston cleanliness, viscosity increase, and filter plugging. It is important to note that technically most of these tests evaluate the combined effectiveness of the detergent

and the dispersant. The performance of the individual additive is hard to unravel. Detergents find additional use in automatic transmission fluids and tractor hydraulic fluids. In this case, the primary function of these additives is not to neutralize acids or to minimize deposit formation, but to alter the frictional properties of these fluids. This is critical if the fluids are to perform effectively as driveline lubricants.

REFERENCES

1. FX Sieloff, JL Musser. What does the engine designer need to know about engine oils? Presented to Detroit Section of the Society of Automotive Engineers, March 16, 1982.
2. A Schilling. *Motor Oils and Engine Lubrication*. London: Scientific Publications, 1968.
3. SQA Rizvi. Additives: chemistry and testing. In *Tribology Data Handbook—An Excellent Friction, Lubrication, and Wear Resource*. Boca Raton, FL: CRC Press, 1997, pp. 117–137.
4. SQA Rizvi. Lubricant additives and their functions. In SD Henry, ed. *Metals Handbook*, Tenth Ed. 1992, pp. 98–112.
5. KU Ingold. Inhibition of autoxidation of organic substances in liquid phase. *Chem Rev* 61:563–589, 1961.
6. SQA Rizvi. Additives and additive chemistry, Accepted for publication in the ASTM Manual on Fuels and Lubricants, to be published by 2003.
7. WC Gergel. Lubricant additive chemistry. Presented at the International Symposium on Technical Organic Additives and Environment, Interlaken, Switzerland, May 24–25, 1984.
8. Process for making overbased calcium sulfonate detergents using calcium oxide and a less than stoichiometric amount of water. U.S. Patent 6,015,778. (1/18/2000, AJ Rolfes and SE Jaynes.).
9. Magnesium low rate number sulphonates. U.S. Patent 5,922,655 (7/13/99, D Moulin, JA Cleverley, and CH Bovington).
10. Method of preparing overbased barium sulfonates. U.S. Patent 3,959,164 (5/25/76), AR SABOL
11. Overbased alkali metal sulfonates. U.S. Patent 4,867,891 (9/19/89, MW Hunt).
12. Metal phenates. U.S. Patent 4,221,673 (9/9/80, R Robson, B Swinney, and RD Tack).
13. Preparation of overbased magnesium phenates. U.S. Patent 4,435,301 (3/6/84, CG Brannen and MW Hunt).
14. Process for the preparation of sulfurized overbased phenate detergents. U.S. Patent 4,973,411 (11/27/90, TC Jao, CK Esche, ED Black, and RH Jenkins, Jr.).
15. Methods for preparing group II metal overbased sulfurized alkylphenols. U.S. Patent 4,971,710 (11/20/90, TV Liston).
16. Production of overbased metal phenates. U.S. patent 4,104,180 (8/1/78, VCE Burnop).
17. Method of preparing overbased lubricating oil additives. U.S. Patent 4,057,504 (11/8/77, M Shiga, K Hirano, M Matsushita).
18. Recovery of overbased alkaline earth metal additives from centrifugates. U.S. Patent 4,910,334 (3/20/90, FA Stuart, WA Tyson, Jr.).
19. Process for preparing overbased naphthenic micronutrient compositions. U.S. Patent 4,243,676 (1/6/81, WR Ali).
20. Process for overbased petroleum oxidate. U.S. Patent 5,013,463 (5/7/91, FJ Slama).
21. Preparation of basic salt. U.S. Patent 4,810,398 (3/7/89, MGA Van Kruchten, RR Van Well).
22. GL Weamer. Additives—A way to quality in motor oils. *Petroleum Refiner* 38:215–219, 1959.

23. Metal salts of organic acids of phosphorus. U.S. Patent 2,785,128 (3/12/57, AH Popkin).
24. Preparation of overbased magnesium sulfonates. U.S. Patent 4,148,740 (4/10/79, VJ Cease, GR Kirk).
25. Basic alkali metal sulfonate dispersions, process for their preparation, and lubricants containing same. U.S. Patent 5,037,565 (8/6/91, LE King).
26. Compounds useful as detergent additives for lubricants and lubricating compositions. U.S. Patent 5,021,174 (6/4/91, P Koch, A Di Serio).
27. ASTM Standards D 482 and D 874, Section 5, Petroleum Products, Lubricants, and Fossil Fuels. 1999 Annual Book of ASTM Standards. American Society of Testing and Materials.
28. ASTM Standard D 974, Section 5, Petroleum Products, Lubricants, and Fossil Fuels. 1993 Annual Book of ASTM Standards. American Society of Testing and Materials.
29. CC Price. The alkylation of aromatic compounds by the Friedel–Crafts method. *Organic Reactions*, Vol III. New York: John Wiley and Sons, 1946, pp 1–82.
30. Alkylation of aromatics with olefins in the presence of an alumina catalyst. U.S. Patent 4,219,690 (8/26/80, SM Kovach).
31. Process and system for alkylation of aromatic compounds. U.S. Patent 5,770,782 (6/23/98, JF Knifton, PR Anantaneni, M Stockton).
32. GA Olah. Friedel–Crafts and related reactions. Vol II. New York: Interscience-Wiley Publishers, 1964.
33. Aromatic alkylation. U.S. Patent 2,754,341 (7/10/56, EV Kirkland).
34. Aromatics alkylation process. U.S. Patent 5,191,135 (3/2/93, FG Dwyer and QN Lee).
35. CM Suter, AW Weston. Direct sulfonation of aromatic hydrocarbons and their halogen derivatives. Chapter 4 in *Organic Reactions*, Vol III. New York: John Wiley and Sons, Inc., 1946, pp 141–197.
36. Conversion of sulfonic acids into a hydrocarbon oil of superior oxidation stability. U.S. Patent 4,188,500 (5/12/80, DS Bosniack, PF Korbach). See “Background of Invention” portion of the patent.
37. KL Kreuz. Gasoline engine chemistry as applied to lubricant problems. *Lubrication* 55:53–64, 1969.
38. KL Kreuz. Diesel engine chemistry as applied to lubricant problems. *Lubrication* 56:77–88, 1970.
39. Alkylation of phenols. Kirk–Othmer Encyclopedia of Chemical Technology, Vol. 1, pp. 894–895, 1963, and Ion exchange, Kirk–Othmer Encyclopedia of Chemical Technology, Vol. II, pp. 871–899. New York: Interscience Publishers, 1967.
40. Manufacture of alkylphenol compounds. U.S. Patent 4,202,199 (5/13/80, F Merger, G Nestler).
41. Methods for preparing alkylated hydroxyaromatics. U.S. Patent 5,663,457 (9/2/97: CJ Kolp).
42. J March, Carboxylation with carbon dioxide, Kolbe–Schmitt reaction. In *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, 4th ed. New York: Wiley-Interscience Publication, 1992. Chapter 11, Section 1–20, pp 546–547.
43. Additives for lubricating oils and processes for producing them. U.S. Patent 5,089,158 (2/18/92, EMGA Van Kruchten, GWJ Heimerikx).
44. Ethylenediamine salts of thiophosphonic acids. U.S. Patent 3,185,728 (5/25/65, EE Schallenberg, RG Lacoste).
45. Olefin-Thionophosphine sulfide reaction products, their derivatives, and use thereof as oil and fuel additives. U.S. Patent 4,042,523 (8/16/77, SJ Brois).
46. NZ Huang. Overbased products using non-ionic substrates—Chemistry and properties. Presented at the Symposium on Recent Advances in the Chemistry of Lubricant Additives, Division of Petroleum Chemistry, National Meeting of the American Chemical Society, New Orleans, August 22–26, 1999.

47. Non-conventional overbased materials. U.S. Patent 5,556,569 (9/17/96, NZ Huang).
48. Sulfurized overbased compositions. U.S. Patent 5,484,542 (1/16/96, JM Cahoon, JL Kara, NZ Haung, JP Roski).
49. Metal complexes and methods of making same. U.S. Patent 2,777,874 (1/15/57, PA Asseff, TW Mastin, A Rhodes).
50. Methods of preparation of superbased salts. U.S. Patent 2,695,910 (11/30/54, PA Asseff, TW Mastin, A Rhodes).
51. Metal-containing lubricant compositions. U.S. Patent 4,767,551 (8/30/88, MW Hunt, S Kennedy).
52. Process for overbasing via metal borate formation. U.S. Patent 6,090,757 (7/18/2000, TF Steckel).
53. Process for overbasing via metal borate formation. U.S. Patent 5,064,545 (11/12/91, TF Steckel).
54. Borated basic metal salt and lubricating oil composition. U.S. Patent 4,539,126 (9/3/85, JJ Bleeker, M Booth, MGFM van Grieken, WJ Krijnen, GD van Wijngaarden).
55. Overbased carboxylate gels, U.S. Patent 5,919,741 (7/6/99, SE Jaynes, WR Sweet).
56. Mixed carboxylate overbased gels. U.S. Patent 5,401,424 (3/28/95, JN Vinci, WR Sweet).
57. Calcium containing micellar complexes. U.S. Patent 3,766,067 (10/16/73, RL McMillen).
58. Magnesium overbasing process. U.S. Patent 5,173,203 (December 22, 1992). (12/22/92, WP Nichols, JL Karn).
59. SQA Rizvi. Additives: Chemistry and testing. In *Tribology Data Handbook—An Excellent Friction, Lubrication, and Wear Resource*. Boca Raton, FL: CRC Press, 1997, pp 117–137.
60. DW Florkowski, TW Selby. The development of a thermo-oxidative engine oil simulation test (TEOST). SAE Technical Paper 932837. Presented at Fuels and Lubricants Meeting and Exposition, Philadelphia, October 18–21, 1993.

Dispersants

SYED Q. A. RIZVI

King Industries, Inc., Norwalk, Connecticut, U.S.A.

1 INTRODUCTION

Lubricants are composed of a base fluid and additives. The base fluid can be mineral, synthetic, or biological in origin. In terms of use, petroleum-derived (mineral) base fluids top the list, followed by synthetic fluids. Base oils of biological origin, that is, vegetable and animal oils, have not gained much popularity except in environmentally compatible lubricants. This is because of the inherent drawbacks these base oils have pertaining to their oxidation stability and low-temperature properties. Additives are added to the base fluid either to enhance an already-existing property, such as viscosity, of a base oil or to impart a new property, such as detergency, lacking in the base oil. The lubricants are designed to perform a number of functions, including lubrication, cooling, protection against corrosion, and keeping the equipment components clean by suspending ordinarily insoluble contaminants in the bulk lubricant [1]. While for automotive applications all functions are important, suspending the insoluble contaminants and keeping the surfaces clean are the most critical. As mentioned in [Chapter 4](#) on *detergents*, this is achieved by the combined action of the detergents and the dispersants present in the lubricant. Dispersants differ from detergents in three significant ways:

1. Dispersants are metal-free, but detergents contain metals, such as magnesium, calcium, and sometimes barium [2]. This means that on combustion detergents will lead to ash formation and dispersants will not.
2. Dispersants have little or no acid-neutralizing ability, but detergents do. This is because dispersants have either no basicity, as is the case in ester dispersants, or low basicity, as is the case in imide/amide dispersants. The basicity of the imide/amide dispersants is due to the presence of

the amine functionality. Amines are weak bases and therefore possess minimal acid-neutralizing ability. Conversely, detergents, especially basic detergents, contain reserve metal bases as metal hydroxides and metal carbonates. These are strong bases, with the ability to neutralize combustion and oxidation-derived inorganic acids, such as sulfuric acid and nitric acid, and oxidation-derived organic acids.

3. Dispersants are much higher in molecular weight, approximately 4–15 times higher, than the organic portion (soap) of the detergent. Because of this, dispersants are more effective in fulfilling the suspending and cleaning functions than detergents.

As mentioned in [Chapter 4](#), dispersants, detergents, and oxidation inhibitors make up the general class of additives called *stabilizers and deposit control agents*. The goal of oxidation inhibitors is to minimize the formation of deposit precursors, such as hydroperoxides and radicals [3,4]. This is because these species are reactive and they attack the hydrocarbon base oil and additives, which make up the lubricant, to form sludge, resin, varnish, and hard deposits. The goal of the dispersant and the soap portion of the detergent is to keep these entities suspended in the bulk lubricant. This not only results in deposit control, but also minimizes particulate-related abrasive wear and viscosity increase. When the lubricant in the equipment is changed, the deposit precursors and the deposit-forming species are removed with the used oil.

The dispersants suspend deposit precursors in oil in a variety of ways. These comprise:

- Including the undesirable polar species into micelles.
- Associating with colloidal particles, thereby preventing them from agglomerating and falling out of solution.
- Suspending aggregates in the bulk lubricant, if they form.
- Modifying soot particles so as to prevent their aggregation. The aggregation will lead to oil thickening, a typical problem in heavy-duty diesel engine oils [5,6].
- Lowering the surface/interfacial energy of the polar species in order to prevent their adherence to metal surfaces.

2 NATURE OF DEPOSITS AND MODE OF THEIR FORMATION

A number of undesirable materials result from the oxidative degradation of various components of the lubricant. These are base oil, additives, and the polymeric viscosity modifier, if present. In engine oils, the starting point for the degradation is fuel combustion, which gives rise to hydroperoxides and free radicals [7]. The compounds in the fuel that are most likely to form peroxides, hydroperoxides, and radicals include highly branched aliphatics, unstaurates, such as olefins, and aromatics, such as alkylbenzenes. All these are present in both gasoline and diesel fuels. ASTM Test Methods D 4420 and D 5186 are used to determine the aromatic content of gasoline and diesel fuels, respectively [8]. The fuel degradation products (peroxides, hydroperoxides, and radicals) go past the piston rings into the lubricant

as blow-by and, because they are highly energetic, attack the largely hydrocarbon lubricant. Again, the highly branched aliphatic, unsaturated, and aromatic structures are among those that are highly susceptible. ASTM Standard D 5292 is commonly used to determine the aromatic content of the base oil [8]. The reaction between the contents of the blow-by and these compounds results in the formation of the lubricant-derived peroxides and hydroperoxides that either oxidatively or thermally decompose to form aldehydes, ketones, and carboxylic acids [3,4,9]. Acids can also result from the high-temperature reaction of nitrogen and oxygen, both of which are present in the air–fuel mixture, the oxidation of the fuel sulfur, and the oxidation, hydrolysis, or thermal decomposition of additives such as zinc dialkyl dithiophosphates. The reaction between nitrogen and oxygen to form NO_x is more prevalent in diesel engines and gasoline engines that are subjected to severe service, such as long-distance driving for extended periods. The NO_x formation initiates when the temperature reaches 137°C [10,11]. Zinc dialkyl dithiophosphates are commonly used as oxidation inhibitors in engine oils [12,13]. All these acids are neutralized by basic detergents to form inorganic metal salts and metal carboxylates. These compounds are of low hydrocarbon solubility and are likely to fall out of solution.

The aldehydes and ketones undergo aldol-type condensation in the presence of bases or acids to form oligomeric or polymeric compounds. These can further oxidize to highly oxygenated hydrocarbons, commonly referred to as *oxygenates*. The oxygenates are usually of sticky consistency, and the term “resin” is often used to describe them [14]. Resin either is the basic component in or is the precursor to all types of deposits. Common types of deposits include varnish, lacquer, carbon, and sludge [15,16]. Varnish, lacquer, and carbon occur when resin separates on hot surfaces and dehydrates and/or polymerizes to make tenacious films. The quantity and the nature of deposits depend on the proximity of the engine parts to the combustion chamber. The parts closer to the combustion chamber, such as exhaust valve head and stem that experience approximate temperatures of $630\text{--}730^\circ\text{C}$ [17,18], will develop carbon deposits. The same is true of the combustion chamber wall, piston crown, top land, and top groove, which are exposed to approximate temperatures of $200\text{--}300^\circ\text{C}$. Carbon deposits are more common in diesel engines than in gasoline engines and result from the burning of the liquid lubricating oil and the high-boiling fractions of the fuel that adhere to hot surfaces [19].

As we move away from these regions to the low-temperature regions, such as the piston skirt, the deposits are not heavy and form only a thin film. For diesel engine pistons, this type of deposit is referred to as “lacquer”; for gasoline engine pistons, this type of deposit is called “varnish”. The difference between lacquer and varnish is that lacquer is lubricant-derived and varnish is largely fuel-derived. In addition, the two differ in their solubility characteristics. That is, lacquer is water-soluble and varnish is acetone soluble [15]. Lacquer usually occurs on piston skirts, on cylinder walls, and in the combustion chamber. Varnish occurs on valve lifters, piston rings, piston skirts, valve covers, and positive crankcase ventilation (PCV) valves.

The coolest parts of the engine, such as rocker arm covers, oil screen, and oil pan, that are exposed to temperatures of $\sim 200^\circ\text{C}$ experience sludge deposits. Sludge can be watery or hard in consistency, depending on the severity of service. If the service is extremely mild and of short duration, as in the case of stop-and-go gasoline

engine operation, the sludge is likely to be watery or mayonnaise-like [15]. This type of sludge is called low-temperature sludge, which occurs when the ambient temperature is below 95°C. The high-temperature sludge is more common in diesel engines and gasoline engines with long, continuous operation. This type of sludge occurs when the ambient temperature is above 120°C and is hard in consistency. In the former case, the engine does not get hot enough to expel combustion water, which stays mixed with oil, imparting sludge, a mayonnaise-like appearance. In the latter case, however, the ambient temperature is high enough to expel water, thereby resulting in hard sludge. Sludge is common in areas that experience low oil flow, such as crankcase bottoms and rocker boxes.

Another component of the combustion effluent that must be considered is soot. Soot not only contributes toward some types of deposits, such as carbon and sludge, but it also leads to a viscosity increase. These factors can cause poor lubricant circulation and lubricating film formation, both of which will result in wear and catastrophic failure. Soot is particulate in nature and results from the incomplete combustion of the fuel and of the lubricating oil from the crankcase that might enter the combustion chamber by traveling past the piston rings [20]. Fuel-derived soot is a chronic problem in the case of diesel engines because diesel fuel contains high-boiling components that do not burn easily. In addition, diesel engine combustion is largely heterogeneous, with poor air–fuel mixing, hence poor combustion [20]. Soot is made of hydrocarbon fragments with some of the hydrogen atoms removed. The particles are charged and hence have the tendency to form aggregates. When aggregates occur on surfaces, such as those of the combustion chamber, soot deposits result. These deposits are soft and flaky in texture. If these occur in oil, lubricant experiences an increase in viscosity. A soot-related viscosity increase usually requires the presence of polar materials in oil that have the ability to associate with soot. These can be additives or polar lubricant oxidation and degradation products. Carbon deposits are lower in carbon content than soot and, in most cases, contain oily material and ash. This makes knowledge of the ash-forming tendency of a lubricant important to a formulator. This concern was addressed in [Chapter 4](#).

When soot associates with resin, one gets either resin-coated soot particles or soot-coated resin particles [16]. The first type of particles results when resin is in excess, and the second type of particles results when soot is in excess. The amount of soot in resin determines the color of the deposits: the higher the soot, the darker the deposits. Sludge results when resin, soot, oil, and water mix [9].

Deposit formation in gasoline engines is initiated by NO_x and oxidation-derived hydroperoxides that react with hydrocarbons in the fuel and the lubricant to form organic nitrates and oxygenates [14,21]. Being thermally unstable, these species decompose and polymerize to form deposits. The deposits typically include resin, varnish, and low-temperature sludge. In diesel engines, however, soot is an important component of the deposits, which include lacquer, carbon deposits, and high-temperature sludge [16]. Typically, carbon deposits are of high metal content, which is mainly due to the presence of detergent additives in the lubricant [22,23].

Detailed mechanism of deposit formation in engines is described elsewhere [24, 25]. The mechanism is based on the premise that both the lubricant and the fuel contribute toward deposit formation. The role of the blow-by, NO_x , and high-temperature oxidative and thermal degradation of the lubricant, described earlier,

is substantiated [24]. The importance of oxygenated precursors—their decomposition, condensation, and polymerization to form deposits—is also supported. The deposit precursors consist of approximately 15 to 50 carbon atoms and contain multiple hydroxy and carboxy functional groups. Because of the polyfunctionality, these molecules have the ability to thermally polymerize to high-molecular-weight products [14,16]. As mentioned earlier, soot associates with polar oxidation products in oil to cause a viscosity increase. Viscosity increase can also occur in gasoline engine oils that have little or no soot. This happens when the oxygen content of the precursors is low and the resulting polymer is of low molecular weight and of good oil solubility [14]. This phenomenon is commonly referred to as *oil thickening* [6]. Conversely, if the oxygen content of the precursors is high, the polymerization results in the formation of high-molecular-weight products of low lubricant solubility. Such products constitute resin, which is of low oil solubility and separates on surfaces. If the surfaces are hot, subsequent dehydration and polymerization lead to the formation of varnish, lacquer, and carbon deposits. It is important to note that deposits are a consequence of lubricant oxidation that accelerates once the oxidation inhibitor package in the lubricant is exhausted.

Three other internal combustion engine problems—oil consumption, ring sticking, and corrosion and wear—are also related to lubricant degradation. Oil consumption is a measure of how much lubricant travels past piston rings into the combustion chamber and burns. A certain minimum amount of the lubricant is necessary in the vicinity of the piston rings to lubricate cylinder walls and/or cylinder liners and hence facilitate piston movement and minimize scuffing. However, if too much lubricant ends up in the combustion chamber, serious emission problems will result. Modern piston designs, such as articulated pistons and pistons with low crevice volume, allow just enough lubricant to minimize scuffing but without adversely contributing to emissions [26,27]. Other parameters that affect oil consumption include the integrity of pistons and the cylinders and the viscosity, volatility, and sealing characteristics of the lubricant. Pistons with stuck rings and out-of-square grooves and cylinders with increased wear will result in a poor seal between the crankcase and the combustion chamber [15]. As a consequence, a larger amount of blow-by will enter the crankcase and increase the rate of lubricant breakdown. This will complicate the situation further. Ring sticking occurs when sticky deposits form in the grooves behind piston rings. This is a serious problem because it not only results in a poor seal, but also leads to poor heat transfer from the cylinder to the wall. If not controlled, this will result in nonuniform thermal expansion of the pistons, loss of compression, and ultimately the failure of the engine [15]. The wear of pistons and the cylinders is undesired for the same reasons. Wear of engine parts is either corrosive or abrasive. *Corrosive wear* arises from the attack of fuel sulfur-derived products, such as sulfur oxides or sulfuric acid, or the acidic byproducts of lubricant oxidation and degradation, such as carboxylic and sulfonic acids. Fuel sulfur-derived piston ring wear and cylinder wear is a serious problem in large, slow-speed marine diesel engines that use a high-sulfur fuel. Corrosive wear is controlled by the use of lubricants with a base reserve, that is, those containing a large quantity of basic detergents. This was discussed in [Chapter 4](#) on detergents. *Abrasive wear* results from the presence of the particulate matter, such as large soot particles, in the lubricant. As described later, dispersants are crucial to the control of soot-related wear.

3 DEPOSIT CONTROL BY DISPERSANTS

Fuel and lubricant oxidation and degradation products, such as soot, resin, varnish, lacquer, and carbon, are of low lubricant (hydrocarbon) solubility, with a propensity to separate on surfaces. The separation tendency of these materials is a consequence of their particle size. Small particles are more likely to stay in oil than large particles. Therefore, resin and soot particles, which are the two essential components of all deposit-forming species, must grow in size via agglomeration prior to separation. Growth occurs either because of dipolar interactions, as is the case in resin molecules, or due to adsorbed polar impurities such as water and oxygen, as is the case in soot particles. Alternatively, soot particles are caught in the sticky resin, which is shown in parts A and B of Figure 1. Dispersants interfere in agglomeration by associating with individual resin and soot particles. The particles with associated dispersant molecules are unable to coalesce because of either steric factors or electrostatic factors [28]. Dispersants consist of a polar group, usually oxygen- or nitrogen-based, and a large nonpolar group. The polar group associates with the polar particles, and the nonpolar group keeps such particles suspended in the bulk lubricant. This is shown in parts C and D of Figure 1. Neutral detergents, or soaps, operate by an analogous mechanism.

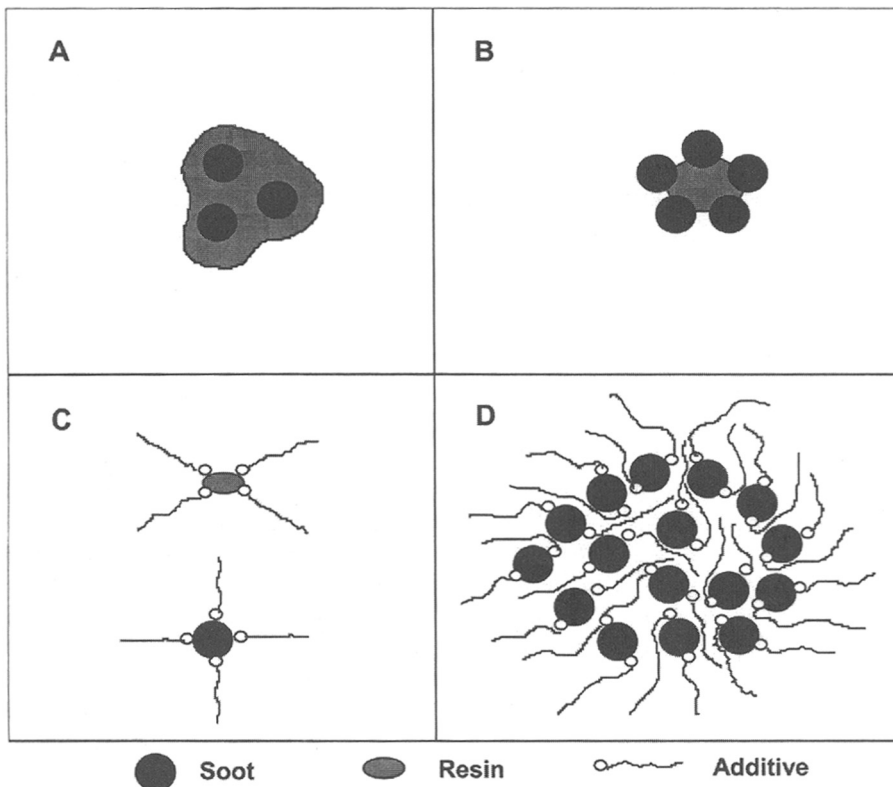


Figure 1 Mechanism of soot-resin-additive interaction. (From Ref. 16.)

4 DESIRABLE DISPERSANT PROPERTIES

Dispersing soot, deposit precursors, and deposits is clearly the primary function of a dispersant. Dispersants, in addition, need other properties to perform effectively. These include thermal and oxidative stability and good low-temperature properties. If a dispersant has poor thermal stability, it will break down, thereby losing its ability to associate with and suspend potentially harmful products. Poor oxidative stability translates into the dispersant molecule contributing itself toward deposit formation. Good low-temperature properties of a lubricant are desired for many reasons: ease of cold cranking, good lubricant circulation, and fuel economy. Base oil suppliers have developed a number of ways to achieve these properties. The methods they use include isomerization of the base stock hydrocarbons via hydrocracking and the use of special synthetic oils as additives. Since dispersant is one of the major components of the engine oil formulations, its presence can adversely affect these properties, which must be preserved.

5 DISPERSANT STRUCTURE

A dispersant molecule consists of three distinct structural features: a *hydrocarbon group*, a *polar group*, and a connecting group or a *link* (see Figure 2). The *hydrocarbon group* is polymeric in nature and, depending on its molecular weight, dispersants can be classified into *polymeric dispersants* and *dispersant polymers*. Polymeric dispersants are of lower molecular weight than dispersant polymers. The molecular weight of polymeric dispersants ranges between 3000 and 7000 as compared to dispersant polymers, which have a molecular weight of 25,000 and higher. While a variety of olefins, such as polyisobutylene, polypropylene, polyalphaolefins, and mixtures thereof, can be used to make polymeric dispersants, the polyisobutylene-derived dispersants are the most common. The number average molecular weight (M_n) of polyisobutylene ranges between 500 and 3000, with an M_n of 1000–2000 being typical [42]. In addition to M_n , other polyisobutylene parameters, such as molecular-weight distribution and the length and degree of branching, are also important in determining the overall effectiveness of a dispersant.

Substances obtained via a polymerization reaction, especially those made by using an acid catalyst or a free-radical initiator, often contain molecules of different sizes. Molecular-weight distribution, or polydispersity index, is commonly used to assess the heterogeneity in molecular size. Polydispersity index is the ratio of weight average molecular weight (M_w) and number average molecular weight (M_n),

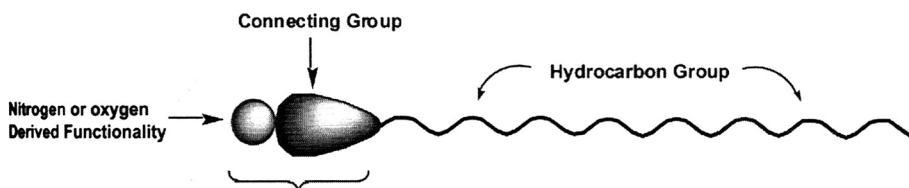


Figure 2 Graphic representation of a dispersant molecule.

or M_w/M_n [29–31]. These molecular weights are determined by subjecting the polymer to gel permeation chromatography (GPC). The method separates molecules based on size [32]. The larger molecules come out first, followed by the next size. When the molecules are of the same size, M_w/M_n equals 1 and the polymer is called a *monodisperse polymer*. The polymers with an index greater than 1 are called *polydisperse polymers*. For most applications, monodispersity is desired. Derived from acid-catalyzed polymerization reaction, polyisobutylene typically has a polydispersity index between 2 and 3. This will impact many of the dispersant properties described below.

Dispersant polymers, also called dispersant viscosity modifiers (DVMs) and dispersant viscosity index improvers (DVIs), are derived from hydrocarbon polymers of molecular weights between 25,000 and 500,000. Polymer substrates used to make DVMs include high-molecular-weight olefin copolymers (OCPs), such as ethylene-propylene copolymers (EPRs), ethylene-propylene-diene copolymers (EPDMs), polymethacrylates (PMAs), styrene-diene rubbers (SDRs) of both linear and star configurations, and styrene-ester polymers (SEs).

The *polar group* is usually nitrogen- or oxygen-derived. Nitrogen-based groups are derived from amines and are usually basic in character. Oxygen-based groups are alcohol-derived and are neutral. The amines commonly used to synthesize dispersants are polyalkylenepolyamines, such as diethylenetriamine and triethylenetetramine. In the case of dispersant viscosity modifiers or dispersant polymers, the polar group is introduced either by direct grafting, copolymerization, or by introducing a reactable functionality. The compounds used for this purpose include monomers, such as 2- or 4-vinylpyridine, *N*-vinylpyrrolidinone, and *N,N*-dialkylaminoalkyl acrylate, and unsaturated anhydrides and acids, such as maleic anhydride, acrylic acid, and glyoxylic acid. The details of these reactions are described in Section 6 of this chapter, which deals with the dispersant synthesis. Amine-derived dispersants are called nitrogen or amine dispersants, and those that are alcohol-derived are called oxygen or ester dispersants [28]. Oxygen-derived phosphonate ester dispersants were popular at one time, but their use in engine oils is now restrained because of the phosphorus limit. Phosphorus limit pertains to its tendency to poison noble metal catalysts used in catalytic converters. Formulators prefer to take advantage of the phosphorus limit by using zinc dialkyl dithiophosphates, which are excellent oxidation inhibitors and antiwear agents. In the case of amine dispersants, it is customary to leave some of the amino groups unreacted to impart basicity to the dispersant. The reasons for this are described later.

6 DISPERSANT SYNTHESIS

Since it is not easy to attach the polar group directly to the hydrocarbon group, except in the case of olefins that are used to make dispersant viscosity modifiers, the need for a connecting group or a link arises. While many such groups can be used, the two common ones are phenol and succinic anhydride. Olefin, such as polyisobutylene, is reacted either with phenol to form an alkylphenol or with maleic anhydride to form an alkenylsuccinic anhydride. The polar functionality is then introduced by reacting these substrates with appropriate reagents.

6.1 The Hydrocarbon Group

Polyisobutylene is the most common source of the hydrocarbon group in polymeric dispersants. It is manufactured via acid-catalyzed polymerization of isobutylene [33,34]. Figure 3 depicts the mechanism of its formation. In the figure polyisobutylene is shown as a terminal olefin, whereas in reality it is a mixture of a variety of isomers. Those that predominate include geminally disubstituted (vinylidene), trisubstituted, and tetrasubstituted olefins. Figure 4 shows their structure and the possible mechanism of their formation. Polyisobutylenes of structures I and II result from the loss of a proton from carbon 1 and carbon 3 of the intermediate of structure V. Polyisobutylenes of structures III and IV result from the rearrangement of the initially formed carbocation, as shown in Figure 4. The reactivity of these olefins toward phenol and maleic anhydride varies. In general, the more substituted the olefin, the lower the reactivity, which is a consequence of the steric factors. Similarly, the larger the size of the polyisobutyl pendant group, that is, the higher the molecular weight, the lower the reactivity. This is due to the dilution effect, which results from low olefin-to-hydrocarbon ratio. As mentioned earlier, polyisobutylene is the most commonly used olefin. One of the reasons for its preference is its extensive branching. This makes the derived dispersants possess excellent oil solubility, in both the nonassociated and associated forms. However, if the hydrocarbon chain in the dispersant is too small, its lubricant solubility greatly suffers. Because of this, the low-molecular-weight components in polyisobutylene are not desired. This is despite their higher reactivity. These must be removed, which is carried out via distillation. Alternatively, one can minimize the formation of these components by decreasing the amount of the catalyst during polymerization and by lowering the polymerization reaction temperature.

A new class of dispersants derived from ethylene/ α -olefin copolymer with an Mn of 300 to 20,000 has also been reported, primarily by the Exxon scientists [35, 36]. Such dispersants are claimed to have superior low-and high-temperature viscometrics than those of the polyisobutylene-derived materials.

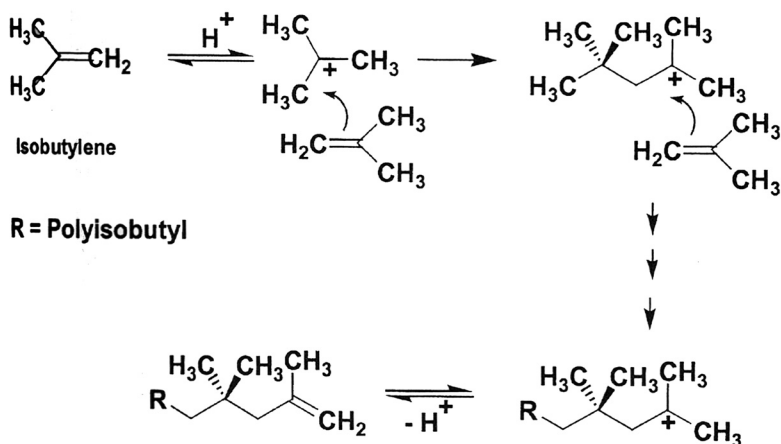


Figure 3 Acid-catalyzed polymerization of isobutylene.

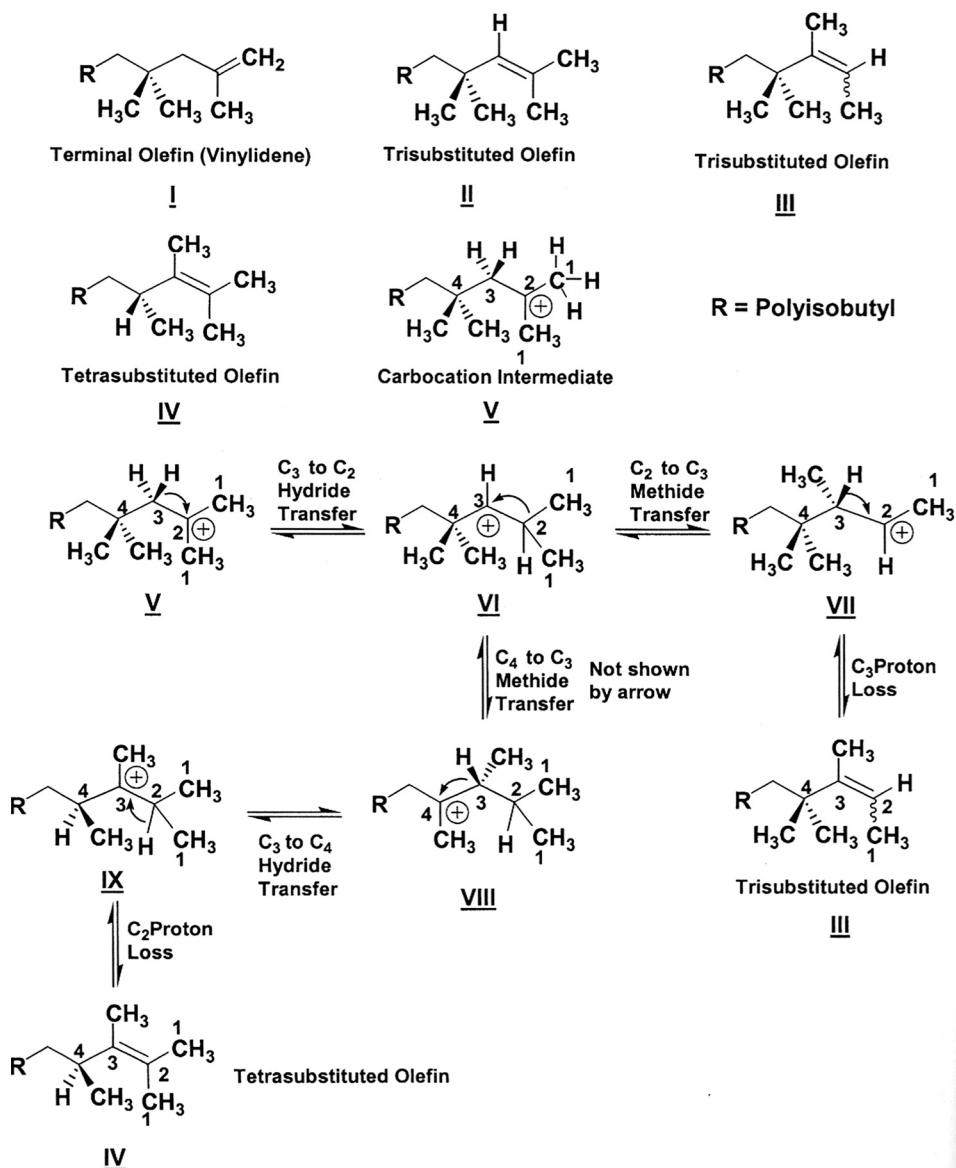


Figure 4 Polyisobutylene structures and the mode of their formation.

As mentioned earlier, dispersant polymers are derived from ethylene-propylene copolymers, styrene-butadiene copolymers, polyacrylates, polymethacrylates, and styrene esters. The ethylene-propylene rubbers are synthesized by Ziegler-Natta catalysis [37]. The styrene-butadiene rubbers are synthesized via anionic polymerization [37]. Polyacrylates and polymethacrylates are synthesized via polymerization of the monomers using free-radical initiators [37]. Styrene esters are made by reacting styrene-maleic anhydride copolymer or styrene-maleic anhydride-alkyl acrylate

terpolymer with alcohols, usually in the presence of a protic acid, such as sulfuric acid or methanesulfonic acid, catalyst. Since complete esterification of the anhydride is hard to achieve, the neutralization of the residual carboxylic acid anhydride is carried out by alternative means [37,38,86].

6.2 The Connecting Group

As mentioned in Section 5, succinimide, phenol, and phosphonate are the common connecting groups used to make dispersants. Of these, succinimide and phenol are the most prevalent [2]. Succinimide group results when a cyclic carboxylic acid anhydride is reacted with a primary amino group. Alkenylsuccinic anhydride is the precursor for introducing the succinimide connecting group in dispersants. Alkenylsuccinic anhydride is synthesized by reacting an olefin, such as polyisobutylene, with maleic anhydride [2]. This is shown in Figure 5.

The reaction is carried out either thermally [40–42] or in the presence of chlorine [43]. The thermal process involves heating the two reactants together [40–42], usually over 200°C. The chlorine-mediated reaction, on the other hand, is carried out by introducing chlorine into the reaction containing polyisobutylene and maleic anhydride [43–47]. Depending on the manner in which the chlorine is added, the procedure is either *one-step* or *two-step* [44]. If the chlorine is first reacted with polyisobutylene prior to adding maleic anhydride, the procedure is considered two-step. If chlorine is added to a mixture of polyisobutylene and maleic anhydride, it is a one-step procedure. The one-step procedure is generally preferred.

The chlorine-mediated process has several advantages, which include having a low reaction temperature, having a faster reaction rate, and working well with internalized or highly substituted olefins. The low reaction temperature minimizes the chances of thermal breakdown of polyisobutylene and saves energy. The major drawback of the chlorine process is that the resulting dispersants contain residual chlorine as organic chlorides. Their presence in the environment is becoming a concern because they can lead to the formation of carcinogenic dioxins. A number of strategies are reported in the literature to decrease the chlorine content in dispersants [48–53]. The thermal process does not suffer from the presence of chlorine, although it is less energy-efficient and requires the use of predominantly a terminal olefin, that is, the polyisobutylene of high vinylidene content.

The mechanism by which the two processes proceed is also different [46,49,50,51]. The thermal process is postulated to occur via an ene reaction. The Chlorine-mediated reaction is postulated to proceed via a Diels–Alder reaction. The mechanism of the diene formation is summarized in Figure 6. The chlorine first

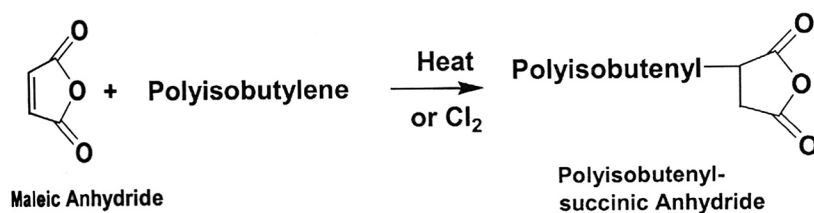


Figure 5 Alkenylsuccinic anhydride formation.

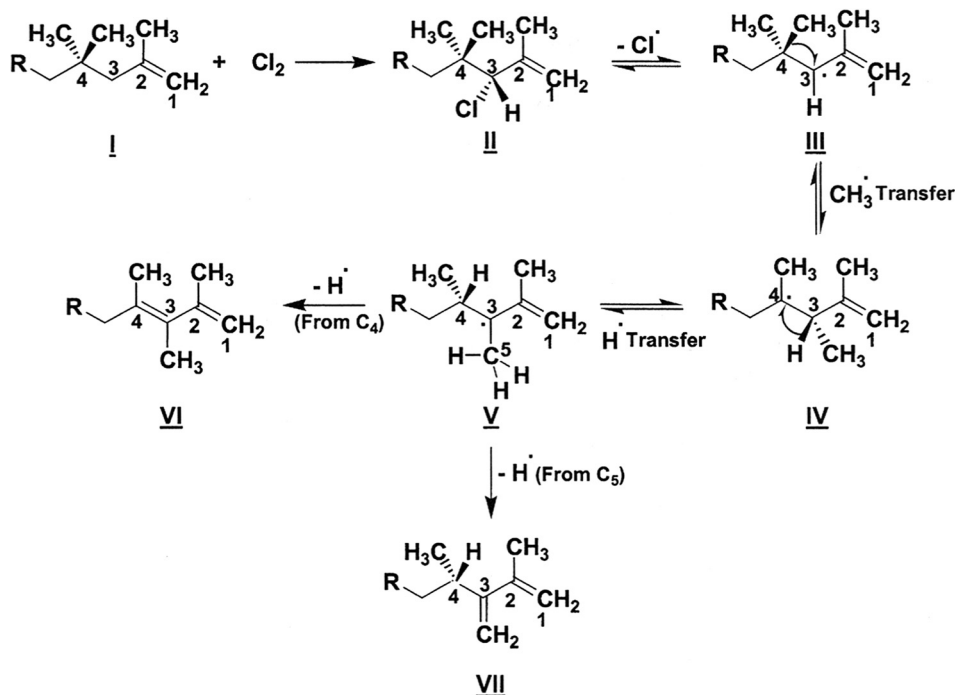


Figure 6 Mechanism of chlorine-assisted diene formation.

reacts with polyisobutylene I to form the allylic chloride II. By the loss of the chloride radical, this yields the intermediate III, which via C_4 to C_3 methyl radical transfer is converted into intermediate IV. A C_3 to C_4 hydrogen shift in the intermediate results in the formation of the radical V. This radical can lose hydrogen either from C_4 to yield the diene VI or from C_5 to result in the diene VII. The resulting dienes then react with maleic anhydride via a 4 + 2 addition reaction, commonly called a Diels–Alder reaction [54], to form alkenyltetrahydrophthalic anhydrides [49,51]. These reactions are shown in Figure 7.

These anhydrides can be converted into phthalic anhydrides via dehydrogenation by the use of sulfur [49–51]. These compounds can then be transformed into dispersants by reacting with polyamines and polyhydric alcohols [50,51]. During the thermal reaction of polyisobutylene with maleic anhydride, that is, the ene reaction, the vinylidene double bond moves down the chain to the next carbon. Since thermal reaction requires a terminal olefin, further reaction of the new olefin with another mole of maleic anhydride will not occur if the double bond internalizes and the reaction will stop at this stage. This is shown in Eq. (3) of Figure 7. If the new double bond is external, the reaction with another molecule of maleic anhydride is possible [45]. This is shown in Eq. (4).

For dispersants, polyisobutylphenol is the alkylphenol of choice. It is synthesized by reacting polyisobutylenes with phenol in the presence of an acid catalyst [55,56]. Lewis acid catalysts, such as aluminum chloride and boron trifluoride, are often employed. Boron trifluoride is preferred over aluminum chloride because the

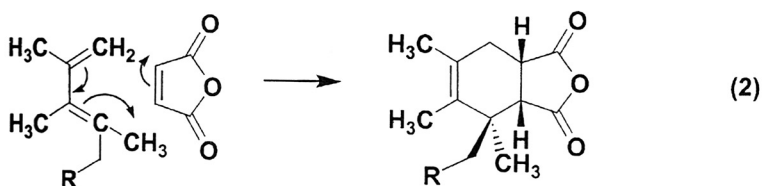
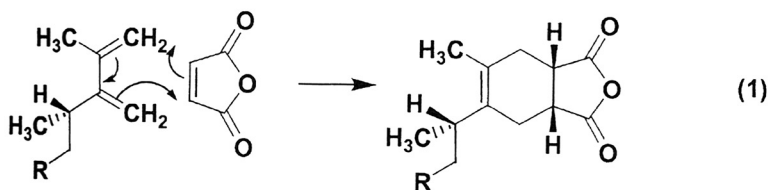
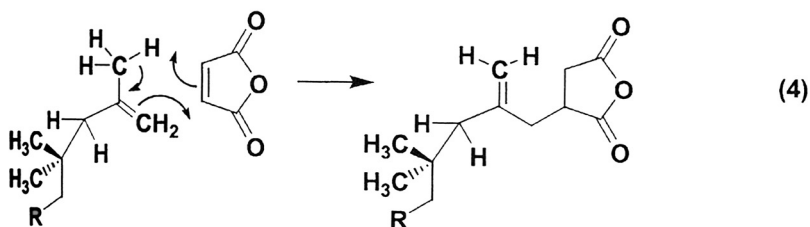
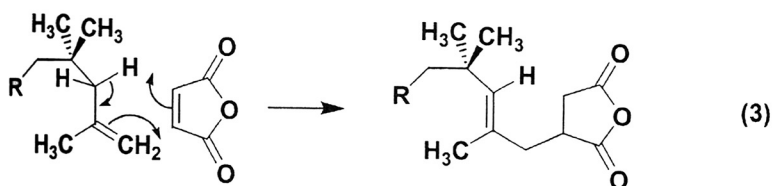
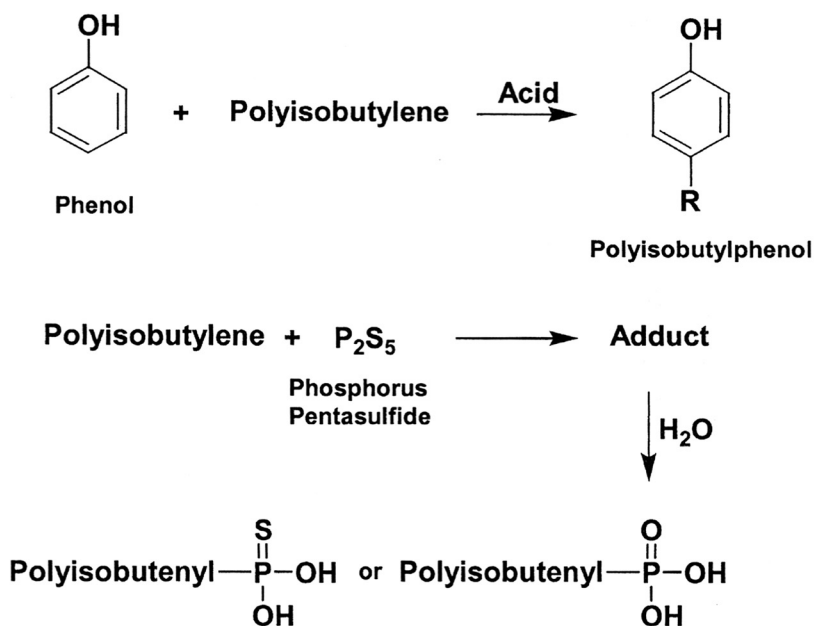
Diels-Alder Reaction**Ene Reaction**

Figure 7 Mechanism of alkenylsuccinic anhydride formation.

reaction can be carried out at low temperatures, which minimizes acid-mediated breakdown of polyisobutylene [56]. This is desired because dispersants derived from low-molecular-weight phenols are not very effective. Other catalysts, such as sulfuric acid, methanesulfonic acid, and porous acid catalysts of Amberlyst® type, can also be used to make alkylphenols [57,58]. Polyisobutylene also reacts with phosphorus pentasulfide via an ene reaction, as described in [Chapter 4](#). The resulting adduct is hydrolyzed by the use of steam to alkenylphosphonic and alkenylthiophosphonic acids [2,3]. The methods to synthesize alkylphenols and alkenylphosphonic acids are summarized in [Figure 8](#).



Polyisobutenylthiophosphonic and Polyisobutenylphosphonic Acids

Figure 8 Synthesis of alkyphenols and alkenylphosphonic acids.

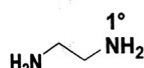
A new carboxylate moiety derived from glyoxylic acid to make dispersants has been reported in the literature [59–63]. However, at present no commercial products appear to be based on this chemistry.

6.3 The Polar Moiety

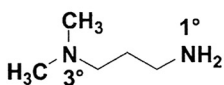
The two common polar moieties in dispersants are based on polyamines and polyhydric alcohols. The structures of common amines and alcohols used to make dispersants are shown in Figure 9.

The polyamines are manufactured from ethylene via chlorination, followed by reaction with ammonia [64]. The reaction scheme is given in Figure 10. As shown, polyamines contain piperazines as a by product. Examining the structures of various amines, one can see that they contain primary amino groups, secondary amino groups, and tertiary amino groups. Each type of amino group has different reactivity toward alkenylsuccinic anhydride. The primary amino group reacts with the anhydride to form a cyclic imide, the secondary amino group reacts with the anhydride to form an amide/carboxylic acid, and the tertiary amino group does not react with the anhydride at all [65].

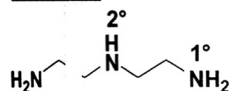
However, it can make a salt if a free carboxylic acid functionality is present in the molecule, as is the case in amide/carboxylic acid. These reactions are shown in Figure 11. New high-molecular-weight amines derived from phosphoric acid-catalyzed condensation of polyhydroxy compounds, such as pentaerythritol, and polyalkylene-polyamines, such as triethylenetetramine, are known [66]. These amines

Diamines

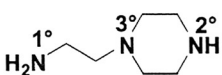
Ethylenediamine



N,N-Dimethylaminopropylamine

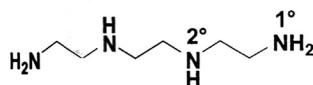
Triamines

Diethylenetriamine

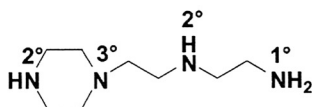


Aminoethylpiperazine

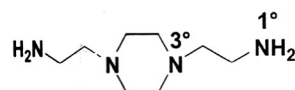
—NH₂ Primary Amino Group (1°)
 Secondary Amino Group (2°)

 Tertiary Amino Group (3°)
Tetramines

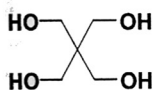
Triethylenetetramine



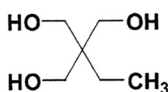
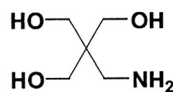
Aminoethylaminoethylpiperazine



Bis(aminoethyl) piperazine

ALCOHOLS

Pentaerythritol

Trimethylolpropane
Tris(hydroxymethyl)propane

Tris(hydroxymethyl)aminoethane

Figure 9 Amines and alcohols used to synthesize dispersants.

are claimed to form high TBN (total base number) dispersants with low free-amine content and better engine test performance than dispersants made from conventional polyamines.

Imide and ester dispersants are made by reacting polyamines and polyhydric alcohols with alkenylsuccinic anhydrides. The reaction typically requires a reaction temperature between 130°C and 200°C to remove the resulting water and complete the reaction [44]. As mentioned earlier, imide dispersants are made by the use of polyalkylene-polyamines, such as diethylenetriamine and triethylenetetramine. Many polyhydric alcohols can be used to make ester dispersants. These include trimethylolpropane, tris(hydroxymethyl)aminoethane, and pentaerythritol. When one

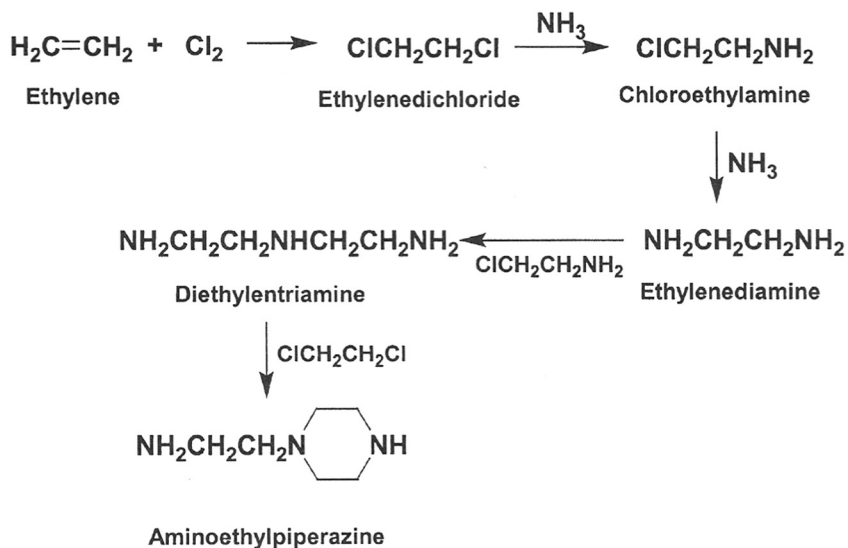
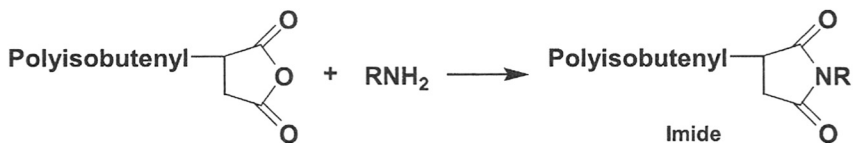
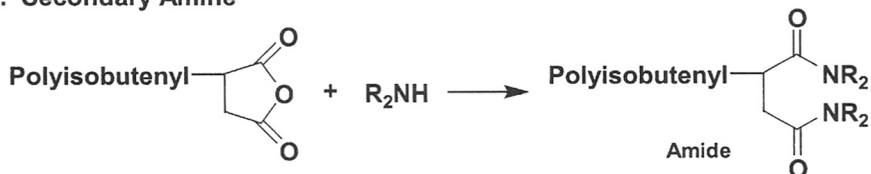


Figure 10 Manufacture of polyamines.

1. Primary Amine



2. Secondary Amine



3. Tertiary Amine

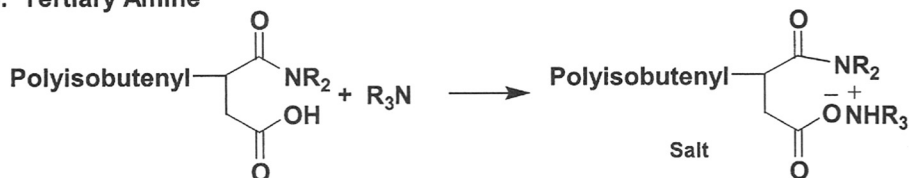


Figure 11 Amine-anhydride reaction products. (Based on Ref. 53.)

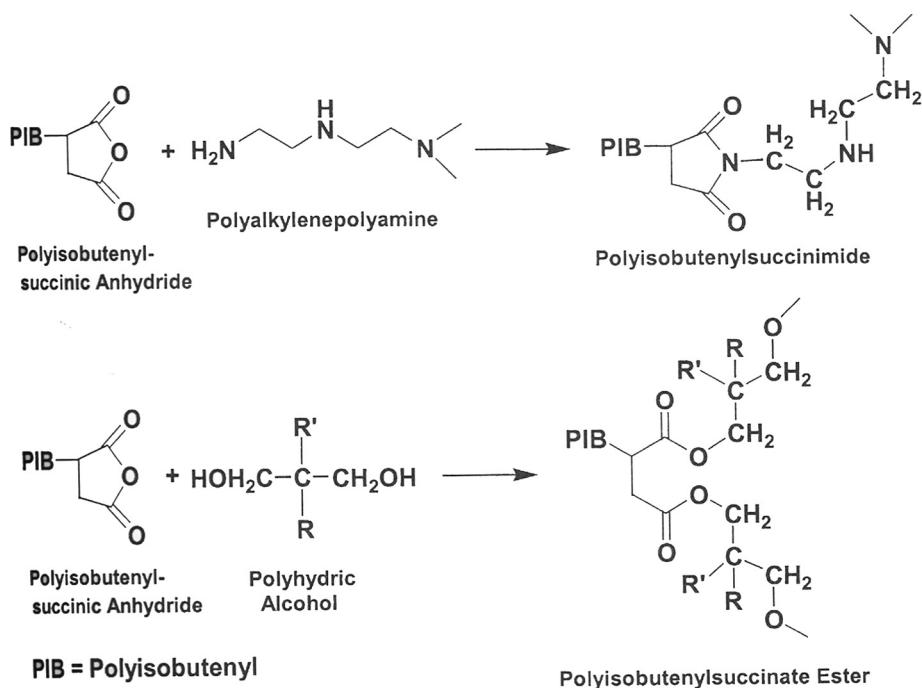


Figure 12 Synthesis of imide and ester dispersants.

uses tris(hydroxymethyl)aminoethane as the alcohol, one can obtain an ester dispersant with basicity. The reaction schemes to make succinimide and succinate dispersants are depicted in Figure 12.

The alkylphenol-derived dispersants are made by reacting an alkylphenol, such as polyisobutylphenol, with formaldehyde and a polyamine [56,67]. The result is the formation of 2-aminomethyl-4-polyisobutylphenol. The reaction of ammonia or an amine, formaldehyde, and a compound with active hydrogen(s), such as a phenol, is called the *Mannich reaction* [68,69]. Hence, such dispersants are called Mannich dispersants. For making phosphonate dispersants, the common method is to react the free acid with an olefin epoxide, such as propylene oxide or butylene oxide, or an amine [2,70,71]. These reactions are summarized in Figure 13. Salts derived from the direct reaction of amine and metal bases with olefin-phosphorus pentasulfide adduct are also known [72,73]. It is important to note that structures in figures are idealized structures. The actual structures will depend on the substrate-(alkylphenol and alkenylsuccinic anhydride) to-reactant (formaldehyde and polyamines) ratio.

Because of the polyfunctionality of the succinic anhydride group and of the amines and the polyhydric alcohols, a variety of dispersants can be made by altering the anhydride-to-amine or anhydride-to-alcohol ratios. These dispersants differ not only in their molecular weight but also in their properties. Polyfunctionality of the two reactants leads to dispersants, which have molecular weights that are 3 to 7 times higher than expected if the two reactants were monofunctional.

The methods to make dispersant viscosity modifiers are shown in Figures 14 to 16. These are synthesized by:

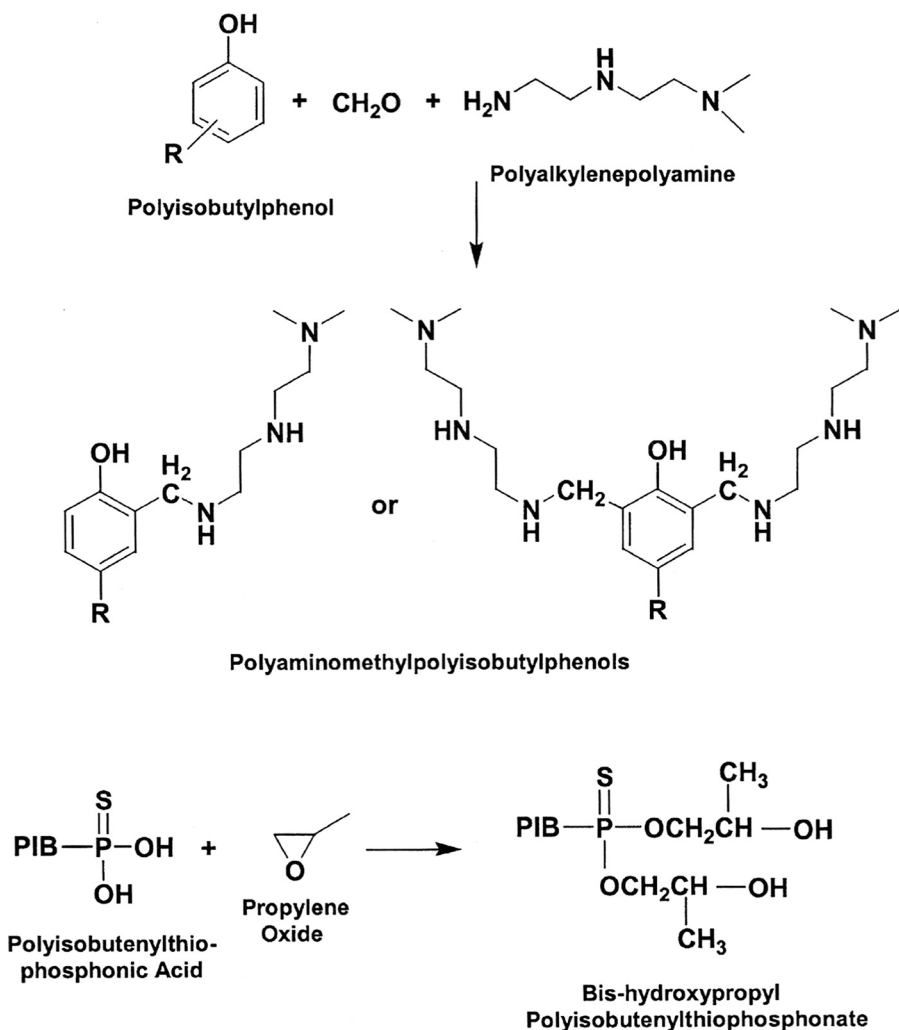


Figure 13 Synthesis of Mannich and phosphonate dispersants.

- Grafting or reacting of a dispersancy-imparting monomer on an already-formed polymer, as in the case of EPRs and SDRs [74–82]
- Including such a monomer during the polymerization process, as in the case of polyacrylates and polymethacrylates [83]
- Introducing a reactive functional group in the polymer that can be reacted with a reagent to impart dispersancy, as in the case of styrene-maleic anhydride copolymers [86–94]

While most of the examples in the figures pertain to introduction of the basic nitrogen-containing moieties, neutral dispersant viscosity modifiers are also known in the literature. These are made by using nonbasic reactants, such as *N*-vinylpyrrolidinone, alcohols, or polyether-derived methacrylate ester [77,84,95]. Recently,

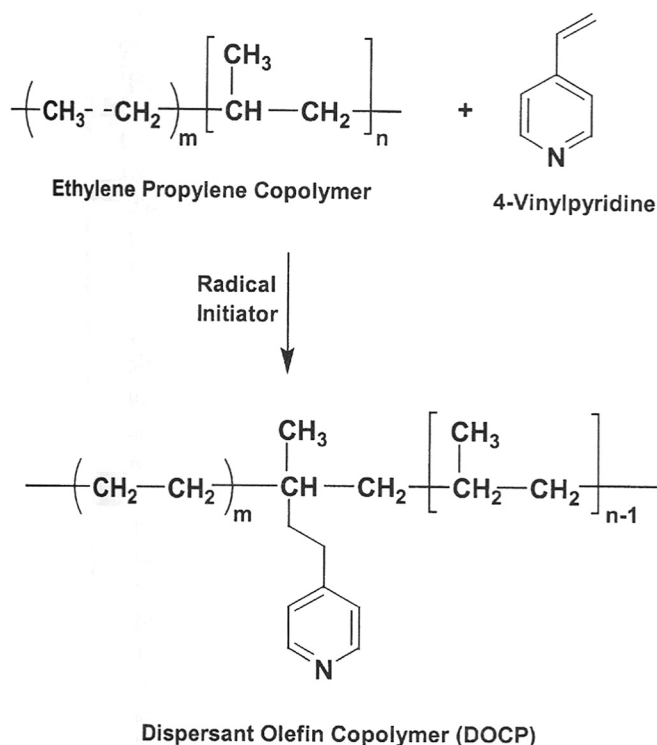


Figure 14 Dispersant viscosity modifier synthesis via grafting.

dispersant viscosity-improving additives with built-in oxidation inhibiting and anti-wear moieties have been reported in the patent literature [75,96,97]. Dispersant polymers containing oxidation-inhibiting moieties are commercially available from Texaco Chemical Company now part of Ethyl Petroleum Additives Company. As the examples show, grafting usually allows the introduction of the connecting group in the dispersant polymers at the same time as the polar moiety.

7 DISPERSANT PROPERTIES

A dispersant consists of a hydrocarbon chain, a connecting group, and a polar functionally. While each structural feature imparts unique properties to a dispersant, the dispersant's overall performance depends on all three. The overall performance is assessed in terms of its dispersancy, thermal and oxidative stability, viscosity characteristics, and seal performance. These criteria primarily relate to engine oils, where dispersants find major use.

7.1 Dispersancy

As mentioned, dispersancy pertains to a dispersant's ability to suspend byproducts of combustion, such as soot, and lubricant degradation, such as resin, varnish, lacquer, and carbon deposits. The overall performance of a dispersant depends on all

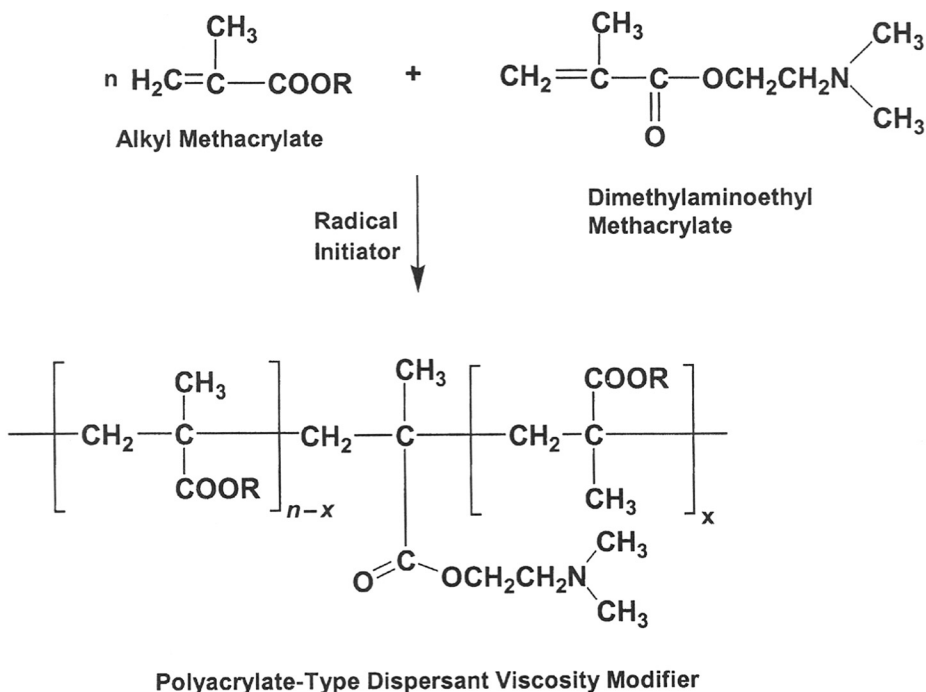


Figure 15 Dispersant viscosity modifier synthesis via copolymerization.

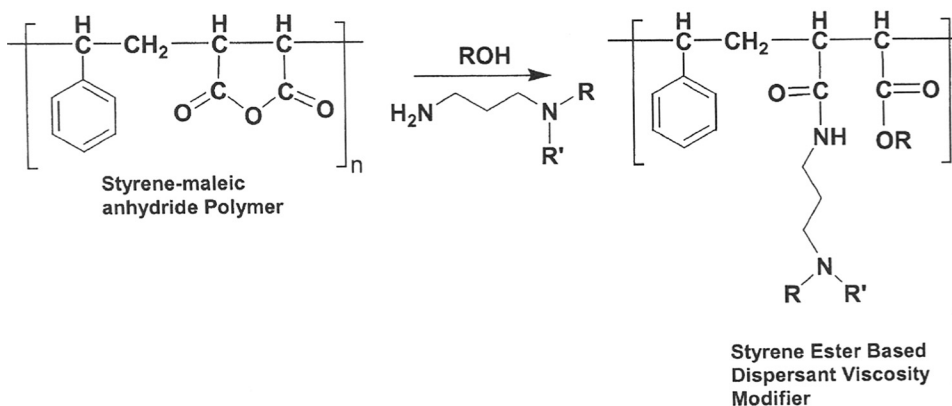


Figure 16 Dispersant viscosity modifier synthesis via chemical reaction.

three of its structural features: the hydrocarbon chain, the connecting group, and the polar moiety. The molecular weight of the hydrocarbon group in a dispersant determines its ability to associate with undesirable polar species and suspend them in the bulk lubricant. For dispersants that have the same connecting group and the polar moiety, the lower the molecular weight, the higher the ability to associate with polar

materials and the lower the ability to suspend them. Because of the tradeoff between the two properties, the hydrocarbon chain must have the correct size and branching.

The size affects a dispersant's affinity toward polar materials, and branching affects its solubility, both before association and after association with the species a dispersant is designed to suspend in oil. Experience has demonstrated that hydrocarbon groups containing 70 to 200 carbon atoms and extensive branching, as in the case of polyisobutylenes, are extremely suitable to design dispersants with good dispersancy. The hydrocarbon chains of larger size, even if the branching is similar, lead to dispersants with low affinity toward polar materials.

That is why dispersant polymers possess lower dispersancy than polymeric dispersants. However, since dispersant polymers have additional attributes, such as good thickening efficiency and in some cases good thermal and oxidative stability, their use is advantageous. They usually replace additives, called viscosity modifiers, in the package. Since they impart some dispersancy because of their structure, the amount of polymeric dispersant in engine oil formulations is decreased somewhat [77,98].

Both the connecting group and the polar moiety are important to the dispersancy of the dispersant molecule. They must be considered together since both contribute toward polarity. In Mannich dispersants, phenol functional group, and in imide and ester dispersants, succinimide, succinate, and phosphonate functional groups are also polar, the same as the amine and the alcohol-derived portion of the molecule. The polarity is a consequence of the electro negativity difference between carbon, oxygen, nitrogen, and phosphorus atoms. The greater the electronegativity difference, the stronger the polarity. This implies that groups that contain phosphorus–oxygen bonds are more polar than those containing carbon–oxygen bonds, carbon–nitrogen bonds, and carbon–phosphorus bonds. The electronegativity difference for such bonds is 1.4, 1.0, 0.5, and 0.4, respectively [99]. However, since dispersants have many bonds with various combinations of atoms, the overall polarity in a dispersant and its ability to associate with polar materials are not easy to predict. Because some of the materials with which the dispersant associates are acidic, such as carboxylic acids derived from lubricant oxidation, the presence of an amine nitrogen is an advantage because of its basic character. Therefore, in certain gasoline engine tests, nitrogen dispersants are superior to ester dispersants. Ester dispersants are usually superior in diesel engine tests because of their higher thermo-oxidative stability. Mannich dispersants are good low-temperature dispersants: hence they are typically used in gasoline engine oils.

As mentioned earlier in the chapter, commercial polyisobutylenes have a molecular-weight distribution. This will lead to dispersant structures of varying size, hence molecular weight. An optimum ratio between the molecular weight of the hydrocarbon chain and that of the polar functionality (polar/nonpolar ratio) is a prerequisite for good dispersancy. If a dispersant composition has an excessive amount of components with short hydrocarbon chains, i.e., of low molecular weight, its associating ability increases, but its oil solubility suffers. This is likely to deteriorate its dispersancy, especially after associating with polar impurities. Such structures in dispersants are, therefore, undesired. Their formation can be minimized by using polyolefins of low polydispersity index, controlling the formation of the low-molecular-weight components, removing such components via distillation [100] or post-reacting with another reagent, preferably of the hydrocarbon type. Polyolefins of

low polydispersity index (≤ 2.0) are available from BP and Exxon Chemical Company. Controlling the formation of the low-molecular-weight components is exemplified by the use of boron trifluoride catalyst for making alkylphenols instead of aluminum chloride, which tends to fragment polyisobutylene. Removing the lower-molecular-weight components, although not easy, is possible at the precursor stage, which is prior to reacting with the alcohol or the amine. A number of reagents can be used for the postreaction [101]. Hydrocarbon post-treatment agents include polyepoxides [102], polycarboxylic acid [103], alkylbenzenesulfonic acids [104], and alkenyl nitriles [105]. Whenever postreacted dispersants are used in engine oils, improved dispersancy, viscosity index credit, improved fluorocarbon elastomer compatibility, hydrolytic stability, and shear stability are often claimed.

7.2 Thermal and Oxidative Stability

All three components of the dispersant structure determine its thermal and oxidative stability, the same as dispersancy. The *hydrocarbon group* can oxidize in the same manner as the lubricant hydrocarbons to form oxidation products that can contribute toward deposit-forming species [4,9]. (This is described in Section 2, on the nature of deposits and mode of their formation.) While the rate of oxidation of largely paraffinic hydrocarbon groups, such as polyisobutyl group, is quite slow, for those that contain multiple bonds, such as polyisobutenyl, and the benzylic groups, it is quite high. The benzylic functional group is present in styrene butadiene- and styrene ester-derived dispersant polymers. Purely paraffinic hydrocarbon groups that contain tertiary hydrogen atoms, such as ethylene-propylene copolymers, oxidize at a faster rate than those that contain only primary and secondary hydrogen atoms. Styrene isoprene-derived materials contain both benzylic and tertiary hydrogen atoms. This implies that highly branched alkyl groups, such as polyisobutyl and polyisobutenyl, have a higher susceptibility toward oxidation than linear or unbranched alkyl groups. Dispersant polymers with built-in oxidation-inhibiting moieties are known in the literature [75,76,96]. The polar moiety in an amine-derived dispersant is also likely to oxidize at a faster rate than the oxygen-derived moiety because of the facile formation of the amine oxide functional group on oxidation. Such groups are known to thermally undergo β -elimination [86], called the *cope reaction*, to form an olefin. This can oxidize at a faster rate as well as lead to deposit-forming polymeric products.

From a thermal stability perspective, the hydrocarbon group in the case of high-molecular-weight dispersant polymers, such as those derived from OCPs, is more likely to break down (unzip) than that derived from the low-molecular-weight polymers. Dispersants based on 1000 to 2000 molecular-weight polyisobutylenes are relatively stable, except at very high temperatures that are experienced in some engine parts, such as near the top of the piston [17,18]. Thermal breakdown of the oxidized amine polar group is mentioned in the previous paragraph.

The chemical reactivity of certain dispersants toward water and other reactive chemicals, present in the lubricant formulation, is an additional concern. The most likely reaction site is the connecting group. The common connecting groups are amide and imide in amine-derived dispersants and ester in alcohol-derived dispersants. All three can hydrolyze in the presence of water [107], but at different rates. Esters are easier to hydrolyze than amides and imides. The hydrolysis is facilitated

by the presence of bases and acids. Basic detergents are the source of the metal carbonate and metal hydroxide bases, which at high temperatures catalyze the hydrolysis reaction. Additives, such as zinc dialkyl dithiophosphates, are a source of strong acids that result when these additives hydrolyze, thermally decompose, or oxidize. The fate of the ester, amide, and imide-type dispersant polymers, such as those derived from polyacrylates, polymethacrylates, and styrene ester substrates, is the same. Some OCP-derived dispersant polymers, such as those obtained by grafting of monomers 2- or 4-vinylpyridine and 1-vinyl-2-pyrrolidinone [74,78], do not suffer from this problem since they do not contain easily hydrolyzable groups. Reactivity toward other chemicals present in the formulation is again prevalent in the case of ester-derived dispersants. Reaction with metal-containing additives, such as detergents and zinc dialkyl dithiophosphates, can occur after hydrolysis to form metal salts. This can destroy the polymeric structure of a dispersant and hence its effectiveness. Some formulations contain amines or their salts as corrosion inhibitors or friction modifiers. Depending on the molecular weight and the ambient temperature, these can displace the polyol or sometimes the polyamine, thereby altering the dispersant structure, hence its properties.

7.3 Viscosity Characteristics

The amount of dispersant in automotive engine oils typically ranges between 3–7% by weight [77], making it the highest among additives. In addition, dispersant is the highest molecular-weight component except the viscosity improver [108]. Both of these factors can alter some physical properties, such as viscosity, of the lubricant. A boost in the viscosity of a lubricant at high temperatures is desired, but at low temperatures it is a disadvantage. At high temperatures, the lubricant loses some of its viscosity [109], hence its film-forming ability, resulting in poor lubrication. Maintaining good high-temperature viscosity of a lubricant is therefore imperative in order to minimize wear damage. This is usually achieved by the use of polymeric viscosity modifiers [3,110]. Some dispersants, especially those that are based on high-molecular-weight polyolefins and have been oversuccinated partly fulfill this need [44]. Therefore, the amount of polymeric viscosity modifier necessary to achieve specific high-temperature viscosity is reduced. Unfortunately, dispersants that provide a viscosity advantage lead to a viscosity increase at low temperatures as well. The low-temperature viscosity requirements for engine oils have two components: *cranking viscosity* and *pumping viscosity* [111]. Cranking viscosity is an indication of how easily the engine will turn over in extremely cold-weather conditions. Pumping viscosity is the ability of the lubricant to be pumped to reach various parts of the engine. For cold-weather operation, low to moderate cranking and pumping viscosities are highly desirable. While pumping viscosity and the pour point can be lowered by the use of additives, called pour point depressants [3,13], lowering cranking viscosity is not easy. In the case of base oils this is usually achieved by blending carefully selected base stocks. An ideal polymeric dispersant must provide high-temperature viscosity advantage without adversely affecting the cold-cranking viscosity of the lubricant. Dispersant polymers have the same requirement. Good high-temperature viscosity to cranking viscosity ratio in polymeric dispersants can be achieved by:

- Carefully balancing the type and the molecular weight of the hydrocarbon chain [112]
- Choosing the optimum olefin-to-maleic anhydride molar ratio [113]
- Selecting the type and the amount of the polyamine used

In dispersant polymers this can be achieved by selecting (1) a polymer of correct molecular weight and branching and (2) a suitable pendent group. Dispersant polymers derived from medium-molecular-weight, highly branched structures, and ester-type pendent groups are best suited for use as additives. Examples include polyacrylate, polymethacrylate, and styrene ester-derived dispersants. These additives not only act as viscosity modifiers and dispersants; they also act as pour point depressants, thereby improving the low-temperature properties of the lubricant.

A number of patents pertaining to dispersants with balanced high-temperature viscosity and low-temperature properties are reported in the patent literature [114–118]. A Mannich (alkylphenol) dispersant, derived from ethylene/1-butene polymers of M_n 1500–7500, has been claimed to possess improved dispersancy and pour point [114]. Another patent claiming the synthesis of a dispersant with superior dispersancy and pour point depressing properties has also been issued [115]. The dispersant is based on the reaction of maleic anhydride/lauryl methacrylate/stearyl methacrylate terpolymer with dimethylaminopropylamine and a Mannich base was obtained by reacting *N*-aminoethylpiperazine, paraformaldehyde, and 2,6-di-*t*-butyl phenol. A number of patents describe the use of ethylene/ α -olefin/diene interpolymers to make dispersants [116–118]. These dispersants are claimed to possess excellent high-temperature and low-temperature viscosities, as defined by VR'/VR . Here VR' pertains to the dispersant and VR pertains to the precursor, such as alkylphenol or alkenylsuccinic anhydride. VR' is the ratio of the -20°C cold-cranking simulator (CCS) viscosity (cP) of a 2% solution of dispersant in a reference oil and the 100°C kinematic viscosity (cSt) of the dispersant. VR is the ratio of the -20°C cold-cranking simulator (CCS) viscosity (cP) of a 2% solution of precursor in the reference oil and the 100°C kinematic viscosity (cSt) of the precursor. The values of 2.0 to 3.9 for VR and VR' and of less than 1.11 for VR'/VR are considered suitable for balanced low- and high-temperature viscosities.

7.4 Seal Performance

Seals in automotive equipment are used for many purposes, the most prominent of which are to have easy access to malfunctioning parts to perform repair and to minimize contamination and the loss of lubricant. A variety of polymeric materials is used to make seals. These include fluoroelastomers, nitrile rubber, polyacrylates, and polysiloxanes (silicones). Maintaining the integrity of seals is critical; otherwise, the lubricant will be lost and wear damage and equipment failure will occur. The seals fail in a number of ways. They can shrink, elongate, or become brittle and thus deteriorate. The damage to elastomer seals is assessed by examining volume, hardness, tensile strength change, and the tendency to elongate and rupture [119]. Two primary mechanisms by which seal damage can occur include abrasion due to particulate matter in the lubricant and the attack of various lubricant components on the seals. The lubricant-related damage can occur when some of its components diffuse into the seals. This will either cause a change in the seal's hardness, thereby leading

to swelling and or elongation, or extract the plasticizer, an agent used to impart flexibility and strength to polymeric materials.

Abrasive damage is not common since most equipment has an installed lubricant filtration system. The lubricant-related damage, however, is of primary interest to us. The lubricant is a blend of base stocks and an additive package. Certain base stocks, such as those of high aromatics content or those that are of ester type, have the tendency to extract the plasticizer because of their high polarity. Additives, on the other hand, have the ability to diffuse into the seal material and alter its properties as well as remove the plasticizer. Among additives, dispersants are the most implicated in causing seal damage, especially to fluoroelastomer (Viton®) seals. While in many cases seal failure can be corrected by the use of additives, called the seal-swell agents, it is wise to eliminate such damage via prevention. Elastomer compatibility requirements are a part of the current U.S., ACEA (Association des Constructeurs Européens de l'Automobile), and Japanese standards for engine oils and worldwide automotive transmission and tractor hydraulic fluid specifications [120]. Damage to seals is prevalent in the case of nitrogen dispersants. In general, the higher the nitrogen content, the higher the seal problems [119]. Rationally, these problems occur due to the presence of low-molecular-weight molecules in the dispersant. These include free amine either as such or in a labile form, such as an alkylammonium salt, or low-molecular-weight succinimides and succinamides. Because of their high polarity and smaller size, these molecules are more likely to diffuse into the seal material and alter its physical and mechanical properties [121]. It is believed that in the case of Viton seals, the loss of fluoride ions is responsible for seal deterioration. Removal of the free amine and of low-molecular-weight succinimides will improve seal performance. Alternatively, one can post-treat dispersants with reagents, such as boric acid and epoxides, which will either make such species innocuous or hinder their diffusion into the seal material. Many chemical treatments of dispersants, covered in the dispersancy section of the chapter, claim to improve seal performance of dispersants and crankcase lubricants that use them. These reagents react with seal-damaging amines and low-molecular-weight succinimides to make them harmless. Strategies other than those listed above are also reported in the patent literature [122–126].

8 PERFORMANCE TESTING

Engine oils account for almost 80% of the automatic transmission dispersant use. Other applications that use these additives include automatic transmission fluids, gear lubricants, hydraulic fluids, and refinery processes as antifoulants. Dispersants of relatively lower molecular weight are also used in fuels to control injector and combustion chamber deposits [127,128]. Such dispersants usually contain a polyether functionality [129].

Succinimide and succinate ester-type polymeric dispersants are used in gasoline and diesel engine oils, but the use of alkylphenol-derived dispersants, that is, of the Mannich type, is limited to gasoline engine oils. Dispersant polymers derived from ethylene-propylene rubbers, styrene-diene copolymers, and polymethacrylates are also used in both gasoline and diesel engine oils. As mentioned earlier, dispersant polymers lack sufficient dispersancy to be used alone and hence are used in combi-

nation with polymeric dispersants. The polymethacrylate and styrene ester-derived dispersant polymers are used in automatic-transmission fluids, in power-steering fluids, and, to a limited extent, in gear oils.

Additive manufacturers use a variety of laboratory screen tests and engine tests to evaluate a dispersant's effectiveness. Many of the screen tests are proprietary, but all are developed around evaluating performance in terms of a dispersant's ability to disperse lamp black or used engine oil sludge. The laboratory engine tests are industry-required tests and include both gasoline engine and diesel engine tests. These are listed in ILSAC (International Lubricant Standardization and Approval Committee), API (American Petroleum Institute), ACEA 2002, JASO (Japanese Automobile Standards Organization), and BIS (Bureau of Indian Standards) standards. It is important to note that the U.S. Military and original equipment manufacturers (OEMs) have their own performance requirements, which are over and above those of the API. While the details of various tests are available in these standards and elsewhere [120], the important engine tests that evaluate a dispersant's performance are listed in Tables 1 to 4.

As mentioned earlier in the chapter, soot-related viscosity increase and deposit-related factors are the primary criteria for evaluating a dispersant's performance. Moreover, as commented in [Chapter 4](#), neutral detergents (soaps) also help control deposits, such as varnish, lacquer, sludge, and carbon. Therefore, besides the control of soot-related viscosity increase, which is the sole domain of dispersants, deposit control is the result of a joint performance of the detergent and the dispersant. However, in this regard the dispersant plays a more prominent role.

Besides engine oils, transmission fluids are the primary users of dispersants. Certain parts of the transmission see very high temperatures, which lead to extensive lubricant oxidation. The oxidation products, such as sludge and varnish, appear on parts; for instance, clutch housing, clutch piston, control valve body, and oil screen components. This can impair the functioning of these parts. A turbohydramatic oxidation test (THOT) is used to determine a transmission fluid's oxidative stability.

Table 1 U.S. Gasoline Engine Tests

Engine test	Engine type	Evaluation criteria
CRC L-38	CLR single-cylinder engine	Bearing corrosion, sludge, varnish, oil oxidation, and viscosity change
ASTM sequence IIIE	1987 Buick V6 engine	Sludge, varnish, wear, and viscosity change
ASTM sequence IIIF	1996 Buick V6 engine	Sludge, varnish, wear, and viscosity change
ASTM sequence VE	Ford Dual-Plug head four-cylinder engine	Sludge, varnish, and wear
ASTM sequence VG TEOST	Ford V8 engine Bench test	Sludge, varnish, and wear Thermal and oxidative stability
High-temperature deposit test	Bench test	High-temperature deposits

Table 2 U.S. Diesel Engine Tests

Engine test	Engine type	Evaluation criteria
Caterpillar 1K	Caterpillar single-cylinder engine	Piston deposits and oil consumption
Caterpillar 1M-PC	Caterpillar single-cylinder engine	Piston deposits and oil consumption
Caterpillar 1N	Caterpillar single-cylinder engine	Piston deposits and oil consumption
Caterpillar 1P	Caterpillar single-cylinder engine	Piston deposits and oil consumption
Mack T-6	Multicylinder engine	Piston deposits, wear, oil consumption, and oil thickening
Mack T-7	Multicylinder engine	Oil thickening
Mack T-8	Multicylinder engine	Oil thickening
Mack T-9	Multicylinder engine	Soot thickening

Table 3 European Gasoline Engine Tests

Engine test	Engine type	Evaluation criteria
ASTM sequence IIIE	Six-cylinder engine	High-temperature oxidation (sludge, varnish, wear, and viscosity increase)
ASTM sequence VE	Four-cylinder engine	Low-temperature sludge, varnish, and wear
Peugeot TU-3M high temperature	Four-cylinder single-point injection engine	Piston deposits, ring sticking, viscosity increase
M-B M111 black sludge	Four-cylinder multipoint injection engine	Engine sludge and cam wear
VW 1302	Four-cylinder carburetted engine	Piston deposits, varnish, wear, and oil consumption
VW T-4	Four-cylinder multipoint injection engine	Extended drain capability

Polymeric dispersants are useful in controlling sludge buildup [130]. When friction modification of the transmission fluid is the goal, either dispersants or their precursors, such as alkenylsuccinic acids or anhydrides, are used in combination with metal sulfonates [131–135]. In many such formulations, the borated dispersant and/or the borated detergent (metal sulfonate) are used.

Dispersants are used in gear oils to improve their properties also. Gear oils usually contain thermally labile extreme-pressure additives. Their decomposition byproducts are highly polar, and dispersants are used to contain them in order to avoid corrosion and deposit formation [136,137]. Polymeric dispersants are used

Table 4 Current European Diesel Engine Tests

Engine test	Engine type	Evaluation criteria
VW 1.6TC diesel intercooler	Four-cylinder engine	Piston deposits, varnish, and ring sticking
VW DI	Four-cylinder direct-injection engine	Piston deposits, viscosity increase, and ring sticking
Peugeot XUD11ATE	Four-cylinder indirect-injection engine	Piston deposits and viscosity increase
Peugeot XUD11BTE	Four-cylinder indirect-injection engine	Piston deposits and viscosity increase
M-B OM 602A	Five-cylinder indirect-injection engine	Engine wear and cleanliness
M-B OM 364A/LA	Four-cylinder direct-injection engine	Bore polishing, piston deposits, varnish, sludge, wear, and oil consumption
M-B OM 441LA	Six-cylinder direct-injection engine	Piston deposits, bore polishing, wear, oil consumption, valve train condition, and turbo deposits
MAN 5305	Single-cylinder engine	Piston deposits, bore polishing, and oil consumption
Mack T-8	Multicylinder engine	Soot-related oil thickening

in hydraulic fluids to overcome wet filtration (AFNOR) problems, which is often required for HF-0 type fluids [138]. Filtration problems occur due to the interaction of water with metal sulfonate detergent and zinc dialkyl dithiophosphate that are used as additives in hydraulic fluid formulations. Fouling is a common problem in many processes, including refinery processes. Fouling refers to the deposition of various inorganic and organic materials, such as salt, dirt, and asphaltenes, on heat transfer surfaces and other processing equipment. This results in poor heat transfer, among other problems. Antifoulants are chemicals used in refinery operations to overcome fouling. Detergents and dispersants are often used for this purpose [139–141].

REFERENCES

1. FX Sieloff, JL. Musser. What does the engine designer need to know about engine oils? Presented to Detroit Section of the Society of Automotive Engineers, March 16, 1982.
2. CC Colyer, WC Gergel. Detergents/dispersants. In RM Mortier, ST Orszulik, eds. *Chemistry and Technology of Lubricants*. New York: CH Publishers, Inc., 1992, pp 62–82.
3. SQA Rizvi. Lubricant additives and their functions. In SD Henry, ed. *American Society of Metals Handbook*, 10th ed. 1992, 18:8–112.
4. KU Ingold. Inhibition of autoxidation of organic substances in liquid phase. *Chemical Rev* 61:563–589, 1961.
5. RE Kornbrenke et al. Understanding soot-mediated oil thickening—Part 6: Base oil effects. SAE Technical Paper 982,665, Society of Automotive Engineers, Oct. 1, 1998.

- Also see parts 1–5 by E Bardasz et al., SAE Papers 952,527 (Oct. 1995), 961,915 (Oct. 1, 1996), 971,692 (May 1, 1997), 976,193 (May 1, 1997), and 972,952 (Oct. 1, 1997).
6. MJ Covitch, BK Humphrey, DE Ripple. Oil Thickening in the Mack T-7 engine test—fuel effects and the influence of lubricant additives on soot aggregation. Presented at SAE Fuels and Lubricants Meeting, Tulsa, OK, Oct. 23, 1985.
 7. EF Obert. *Internal Combustion Engines and Air Pollution*. New York: Intext Educational Publishing, 1968.
 8. Petroleum products, lubricants, and fossil fuels. *Annual Book of Standards*. Philadelphia: American Society of Testing and Materials, 1998.
 9. J Cochrac, SQA Rizvi. Oxidation and oxidation inhibitors. Accepted for publication in the ASTM Manual on Fuels and Lubricants, to be published in 2003.
 10. Gas and expansion turbines. In DM Considine, ed. *Van Nostrand's Scientific Encyclopedia*. 5th ed. New York: Van Nostrand Reinhold, 1976, pp 1138–1148.
 11. YB Zeldovich, PY Sadovnikov, DA Frank-Kamenetskii. *Oxidation of Nitrogen in Combustion*. Moscow-Leningrad: Academy of Sciences, U.S.S.R., 1947.
 12. JF Ford. Lubricating oil additives—a chemist's eye view. *J Institute of Petroleum* **54**:188–210, July 1968.
 13. SQA Rizvi. Additives: Chemistry and testing. In *Tribology Data Handbook—an Excellent Friction, Lubrication, and Wear Resource*. Boca Raton, FL: CRC Press, 1997. pp 117–137.
 14. KL Kreuz. Gasoline engine chemistry as applied to lubricant problems. *Lubrication* **55**: 53–64. 1969.
 15. CA Bouman. *Properties of Lubricating Oils and Engine Deposits*. London: McMillan and Co., 1950, pp 69–92.
 16. KL Kreuz. Diesel engine chemistry as applied to lubricant problems. *Lubrication* **56**:77–88. 1970.
 17. WB Chamberlin, JD Saunders. Automobile engines. In RE Booser, ed. *CRC Handbook of Lubrication, Vol. I, Theory and Practice of Tribology: Applications and Maintenance*. Boca Raton, FL: CRC Press, 1983, pp 3–44.
 18. EF Obert. Basic engine types and their operation. In *Internal Combustion Engines and Air Pollution*. New York: Intext Educational Publishing, 1968, pp 1–25.
 19. A Schilling. Antioxidant and anticorrosive additives. In *Motor Oils and Engine Lubrication*. London: Scientific Publications, 1968. Section 2.8, p 2.61.
 20. Patterson, NA Henein. *Emissions from Combustion Engines and Their Control*. Ann Arbor, MI: Ann Arbor Science Publishers, 1972.
 21. DR Lachowicz, KL Kreuz. Peroxynitrates. The unstable products of olefin nitration with dinitrogen tetroxide in the presence of oxygen. A new route to α -nitroketones. *J Organic Chemistry* **32**:3885–3888, 1967.
 22. MJ Covitch, RT Graf, DT Gundic. Microstructure of Carbonaceous Diesel Engine Piston Deposits. *Lubricant Engineering* **44**:128, 1988.
 23. MJ Covitch, JP Richardson, RT Graf. Structural aspects of European and American diesel engine piston deposits. *Lubrication Science* **2**:231–251, 1990.
 24. WM Nahamuck, CW Hyndman, SA Cryvoff. Development of the PV-2 engine deposit and wear test. An ASTM Task Force Progress Report, SAE Publication 872,123. Presented at International Fuels and Lubricants Meeting and Exposition. Toronto, Canada, Nov. 2–5, 1987.
 25. M Rasberger. Oxidative degradation and stabilization of mineral oil based lubricants. In RM Mortier, ST Orszulik, eds. *Chemistry and Technology of Lubricants*. New York: VCH Publishers, Inc., 1992, pp 83–123.
 26. CR Oliver, RM Reuter, JC Sendra. Fuel efficient gasoline-engine oils. *Lubrication* **67**: 1–12, 1981.

27. R Stone. Introduction to Internal Combustion Engines, Society of Automotive Engineers, 1993.
28. SQA Rizvi. Additives and additive chemistry. Accepted for publication in the ASTM Manual on Fuels and Lubricants, to be published in 2003.
29. AR Cooper. Molecular weight determination. In JI Kroschwitz, ed. Concise Encyclopedia of Polymer Science and Engineering. New York: Wiley Interscience, 1990, pp 638–639.
30. A Ravve. Molecular weights of polymers. In Organic Chemistry of Macromolecules. New York: Marcel Dekker, 1967, pp 39–54.
31. RD Deanin. Polymer Structure, Properties, and Applications. New York: Cahner Books, 1972, p 53.
32. JC Randall. Microstructure. In JI Kroschwitz, ed. Concise Encyclopedia of Polymer Science and Engineering. New York: Wiley Interscience, 1990, p 625.
33. JD Fotheringham. Polybutenes. In LR Rudnick, RL Shubkin, eds. Synthetic Lubricants and High-Performance Functional Fluids, 2nd ed. New York: Marcel Dekker, 1999.
34. SJ Randles et al. Synthetic base fluids. In RM Mortier, ST Orszulik, eds. Chemistry and Technology of Lubricants. New York: VCH Publishers, 1992, 32–61.
35. Ethylene alpha-olefin polymer substituted mono-and dicarboxylic acid dispersant additives, U.S. Patent 5,435,926 (7/25/95, A Gutierrez, RA Kleist, WR Song, A Rossi, HW Turner, HC Welborn, RD Lundberg).
36. Novel ethylene alpha-olefin copolymer substituted mannich base lubricant dispersant additives. U.S. Patent 5,017,299 (5/21/91, A Gutierrez, WR Song, RD Lundberg, RA Kleist).
37. RL Stambaugh. Viscosity index improvers and thickeners. In RM Mortier, ST Orszulik, eds. Chemistry and Technology of Lubricants. New York: VCH Publishers, 1992.
38. Nitrogen-containing esters and lubricants containing them. U.S. Patent 4,604,221 (8/5/86, CP Bryant, HM Gerdes).
39. Nitrogen-free ester of carboxy containing interpolymers. U.S. Patent 5,256,752 (10/26/93, DM Dishong, RM Lange).
40. Lubricating oils containing metal derivatives. U.S. Patent 2,628,942 (2/17/53, JR Morris, R Roach).
41. Modified olefin-diolefin resin. U.S. Patent 2,634,256 (4/7/53, WJ Sparks, DW Young, Roselle, JD Garber).
42. Lubricating-oil compositions containing alkenyl succinimides of tetraethylene pentamine. U.S. Patent 3,361,673 (1/2/68, FA Stuart, RG Anderson, AY Drummond).
43. Reaction product of high molecular weight succinic acids and succinic anhydrides with an ethylene polyamine. U.S. Patent 3,172,893 (3/9/65, WM Le Suer, GR Norman).
44. Novel carboxylic acid acylating agents, derivatives thereof, concentrate and lubricant compositions containing the same, and processes for their preparation. U.S. Patent 4,234,435 (11/18/80, NA Meinhardt, KE Davis).
45. Lubricant. U.S. Patent 3,215,707 (11/2/65, RJ Rense).
46. J Weill, B Sillion. Reaction of chlorinated polyisobutene with maleic anhydride: Mechanism of catalysis by dichloromaleic anhydride. *Revue de l'Institut Francais du Petrole* **40**(1): 77–89, 1985. Also see J. Weill's Ph. D. dissertation (1982).
47. Process for manufacturing anhydrides of alkenyl dicarboxylic acids. U.S. Patent 4,433,157 (2/21/84, J Weill, J Garapon, B Sillion).
48. Treatment of organic compounds to reduce chlorine level. U.S. Patent 5,708,097 (1/13/98, CK Baumanis, MM Maynard, AC Clark, MR Sivik, CP Kovall, DL Westfall).

49. Low chlorine polyalkylene substituted carboxylic acylating agent compositions and compounds derived therefrom. U.S. Patent 5,885,944 (3/23/99, JK Pudelski, MR Sivik, KF Wollenberg, R Yodice, J Rutter, JG Dietz).
50. Low chlorine content composition for use in lubricants and fuels. U.S. Patent 6,077,909 (6/20/2000, JK Pudelski, CJ Kolp, JG Dietz, CK Baumanis, SL Bartley, JD Burrington).
51. KF Wollenberg, JK Pudelski. Preparation, NMR characterization and lubricant additive application of novel polyisobutenyl phthalic anhydrides. Symposium on Recent Advances in the Chemistry of Lubricant Additives. Paper presented before the Division of Petroleum Chemistry, Inc., 218th National Meeting of the American Chemical Society, New Orleans, LA, Aug. 22–26, 1999.
52. One-step process for the preparation of alkenyl succinic anhydride. U.S. Patent 5,319,030 (6/7/94, JJ Harrison, R Ruhe, Jr., R William).
53. Two-step thermal process for the preparation of alkenylsuccinic anhydride. U.S. Patent 5,625,004 (4/29/97, JJ Harrison, R Ruhe, Jr., R William).
54. RT Morrison, RN Boyd. The Diels–Alder reaction. In *Organic Chemistry*, 3rd ed. Boston: Allyn and Bacon, 1976, Section 27.8, pp 876–878.
55. Alkylation of phenols. Kirk-Othmer Encyclopedia of Chemical Technology, vol. 1. 1963, pp. 894–895; and Ion exchange. Kirk-Othmer Encyclopedia of Chemical Technology, vol. II. New York: Interscience Publishers, 1967, pp 871–899.
56. Aromatic Mannich compound-containing composition and process for making same. U.S. Patent 6,179,885 (1/30/2001, JR McAtee).
57. Manufacture of alkylphenol compounds. U.S. Patent 4,202,199 (5/13/80, F Merger, G Nestler).
58. Methods for preparing alkylated hydroxyaromatics. U.S. Patent 5,663,457 (9/2/97, CJ Kolp).
59. Hydroxy-group containing acylated nitrogen compounds useful as additives for lubricating oil and fuel compositions. U.S. Patent 5,696,067 (12/9/97, PE Adams, MR Baker, JG Dietz).
60. Mixed carboxylic compositions and derivatives and use as lubricating oil and fuel. U.S. Patent 6,030,929 (2/29/2000, JK Pudelski).
61. Substituted carboxylic acylating agent compositions and derivatives thereof for use in lubricants and fuels. U.S. Patent 5,912,213 (6/15/99, MR Baker, JG Dietz, R Yodice).
62. Acylated nitrogen compounds useful as additives for lubricating oil and fuel compositions. U.S. Patent 5,856,279 (1/5/99, MR Baker).
63. Process for preparing condensation product of hydroxy-substituted aromatic compounds and glyoxylic reactants. U.S. Patent 6,001,781 (12/14/99, MR Baker, KM Hull, DL Westfall).
64. Ethylene amines. In Kirk Othmer's Encyclopedia of Chemical Technology, 2nd ed. vol. 7. New York: Interscience Publishers, 1965, pp 22–37.
65. RT Morrison, RN Boyd. Amines II. Reactions. *Organic Chemistry*, 3rd ed. Boston: Allyn and Bacon, 1976, pp 745–748.
66. High molecular weight nitrogen-containing condensates and fuels and lubricants containing same. U.S. Patent 5,053,152 (10/1/91, TF Steckel).
67. Dispersants and process for their preparation. U.S. Patent 3,980,569 (9/14/76, JF Pindar, JM Cohen, CP Bryant).
68. Artificial resins and method of making. U.S. Patent 2,098,869 (11/9/37, J Harmon, FM Meigs).
69. J March. Aminoalkylation and amidoalkylation. In *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, 4th ed. New York: Wiley-Interscience, 1992, pp 550–551.

70. Ethylenediamine salts of thiphosphonic acids. U.S. Patent 3,185,728 (5/25/65, EE Schallenberg, RG Lacoste).
71. Friction reducing agents for lubricants. U.S. Patent 3,702,824 (11/14/72, RC Schlicht).
72. Olefin-thionophosphine sulfide reaction products, their derivatives, and use thereof as oil and fuel additives. U.S. Patent 4,042,523 (8/16/77, SJ Brois).
73. Olefin-thionophosphine sulfide reaction products, their derivatives, and use thereof as oil and fuel additives. U.S. Patent 4,100,187 (7/11/78, SJ Brois).
74. Oil containing dispersant VII olefin copolymer. U.S. Patent 4,715,975 (12/29/87, MM Kapuscinski, BJ Kaufman, CS Liu).
75. Dispersant-antioxidant multifunction viscosity index improver. U.S. Patent 4,699,723 (10/13/87, MM Kapuscinski, RE Jones).
76. Dispersant anti-oxidant VI improver and lubricating oil composition containing same. U.S. Patent 4,948,524 (8/14/90, MM Kapuscinski, TE Nalesnik, RT Biggs, H Chafetz, CS Liu).
77. Lubricant for use in diesel engines. U.S. Patent 6,187,721 (2/13/2001, I Goldblatt, M McHenry, K Henderson, D Carlisle, N Ainscough, M Brown, R Tittel).
78. Graft copolymers and lubricants containing such as dispersant-viscosity improvers. U.S. Patent 5,298,565 (3/29/94, RM Lange, CV Luciani).
79. Dispersant viscosity index improvers. U.S. Patent 6,083,888 (7/4/2000, RJ Sutherland).
80. Lubricating oils and fuels containing graft copolymers. U.S. Patent 3,506,574 (4/14/70, RL Stambaugh, RD Bakule).
81. Viscosity index improvers with dispersant properties prepared by reaction of lithiated hydrogenated copolymers with 4-substituted aminopyridines. U.S. Patent 4,402,843 (9/6/83, WJ Trepka).
82. Viscosity index improvers with dispersant properties prepared by reaction of lithiated hydrogenated copolymers with substituted aminolactams. U.S. Patent 4,402,844 (9/6/83, WJ Trepka).
83. Viscosity improvers for lubricating oil composition. U.S. Patent 6,124,249 (9/26/2000, JG Seebauer, CP Bryant).
84. Dispersant-viscosity improvers for lubricating oil compositions. U.S. Patent 5,969,068 (10/19/99, CP Bryant, BA Grisso, R Cantiani).
85. Dispersant-viscosity improvers for lubricating oil compositions. U.S. Patent 5,821,313 (10/13/98, MR Sivik, CP Bryant).
86. Lubricating oil additives. U.S. Patent 6,071,862 (6/6/2000, JR Shanklin, Jr., NC Mathur).
87. Intermediates useful for preparing dispersant-viscosity improvers for lubricating oils. U.S. Patent 6,117,941 (9/12/2000, PE Adams, RM Lange, R Yodice, MR Baker, JG Dietz).
88. Dispersant-viscosity improves for lubricating oil composition. U.S. Patent 5,512,192 (4/30/96, RM Lange, CV Luciani).
89. Dispersant-viscosity improvers for lubricating oil compositions. U.S. Patent 5,540,851 (7/30/96, R M Lange).
90. Graft copolymers from solvent-free reactions and dispersant derivatives thereof. U.S. Patent 5,429,758 (7/4/95, K Hayashi, TR Hopkins, CR Scharf).
91. Novel VI improver, dispersant, and anti-oxidant additive and lubricating oil composition containing same. U.S. Patent 4,863,623 (9/5/89, TE Nalesnik).
92. Functionalized graft co-polymer as a viscosity index improver, dispersant, and anti-oxidant additive and lubricating oil composition containing same. U.S. Patent 5,409,623 (4/25/95, MK Mishra, ID Rubin).
93. Lubricating oil containing dispersant viscosity index improver. U.S. Patent 5,520,829 (5/28/96, MK Kapuscinski, CS Liu, LD Grina, RE Jones).

94. Process for making dispersant viscosity index improvers. U.S. Patent 5,486,563 (1/23/96, RJ Sutherland).
95. Star-shaped dispersant viscosity index improver. U.S. Patent 4,077,893 (3/7/78, TE Kiovsky).
96. Multifunctional viscosity index improver-dispersant antioxidant. U.S. Patent 5,439,607 (8/8/95, AO Patil).
97. Lubricants containing ashless antiwear-dispersant additive having viscosity index improver credit. U.S. Patent 5,698,5000 (12/16/97, JR Baranski, CA Migdal).
98. Dispersant viscosity index improvers. U.S. Patent 5,360,564 (11/1/94, RJ Sutherland, RB Rhodes).
99. JE Brady, GE Humiston. Chemical bonding: General concepts—polar molecules and electronegativity. In *General Chemistry: Principles and Structure*, 2nd ed. New York: John Wiley and Sons, 1978, pp 114–117.
100. Dispersant additives and process. U.S. Patents 5,804,667 (9/8/98) and 5,936,041 (8/10/99, WB Diana, JV Cusumano, KR Gorda, J Emert, WB Eckstrom, DC Dankworth, JE Stanat, JP Stokes).
101. Ashless dispersants formed from substituted acylating agents and their production and use. U.S. Patent 5,241,003 (8/31/93, DJ Degonia, PG Griffin).
102. Oil soluble dispersant additives useful in oleaginous compositions. U.S. Patent 5,026,495 (6/25/91, J Emert, RD Lundberg, A Gutierrez).
103. Middle distillate containing storage stability additive. U.S. Patent 4,948,386 (8/14/90, RL Sung, BJ Kaufman, KJ Thomas).
104. Non-ash containing lubricant oil composition. U.S. Patent 3,189,544 (6/15/65, H Ratner, RF Bergstrom).
105. Reaction products of hydrocarbon-substituted succinic acid-producing compound, an amine, and an alkenyl cyanide. U.S. Patents 3,278,550 (10/11/66) and 3,366,569 (6/30/68, GR Norman, WM Le Suer).
106. J March. Cleavage of amine oxides. In *Advanced Organic Chemistry*, 4th ed. New York: Wiley-Interscience Publication, 1992, pp 1018–1019.
107. RT Morrison, RN Boyd. Hydrolysis of amides, pp 671–672, and Alkaline and acidic hydrolysis of esters, pp 677–681. In *Organic Chemistry*, 3rd ed. Boston: Allyn and Bacon, 1976.
108. SK Baczek, WB Chamberlin. Petroleum additives. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed., vol. 11. New York: John Wiley and Sons, 1998, p 22.
109. D Klamann. Viscosity-temperature (VT) function. In *Lubricants and Related Products*. Weinheim, Germany: Verlag Chemie, 1984, pp 7–12.
110. A Schilling. Viscosity index improvers. In *Motor Oils and Engine Lubrication*. London: Scientific Publications, 1968, pp 2.28–2.43.
111. Engine oil viscosity classification. SAE J300—Revised December 1999, SAE Standard, Society of Automotive Engineers.
112. Multigrade lubricating compositions containing no viscosity modifier. U.S. Patent 5,965,497 (10/12/99, DR Adams, P Brice).
113. High functionality low molecular weight oil soluble dispersant additives useful in oleaginous compositions. U.S. Patent 5,788,722 (8/4/98, J Emert, RD Lundberg).
114. Polymers derived from ethylene and 1-butene for use in the preparation of lubricant dispersant additives. U.S. Patent 6,030,930 (2/29/2000, J Emert, A Rossi, S Rea, JW Frederick, MW Kim).
115. Lubricating oil containing dispersant VII and pour depressant. U.S. Patent 4,668,412 (5/26/87, WP Hart, CS Liu).
116. Ethylene alpha-olefin/diene interpolymersubstituted carboxylic acid dispersant additives. U.S. Patents 5,759,967 (6/2/98) and 5,681,799 (10/28/97, WR Song, A Rossi, HW Turner, HC Welborn, RD Lundberg, A Gutierrez, RA Kleist).

117. Ethylene alpha-olefin polymer substituted mono-and dicarboxylic acid dispersant additives. U.S. Patent 5,433,757 (7/18/95, WR Song, A Rossi, HW Turner, HC Welborn, RD Lundberg).
118. Borated ethylene alpha-olefin copolymer substituted Mannich base lubricant dispersant additives. U.S. Patent 5,382,698 (1/17/95, WR Song, RD Lundberg, A Gutierrez, RA Kleist).
119. Polyalkylene polysuccinimides and post-treated derivatives thereof. U.S. Patent 6,146,431 (11/14/2000, JJ Harrison, WA Ruhe, Jr.).
120. Ready reference for lubricant and fuel performance. Lubrizol Publication. Available at Lubrizol.com Internet web page.
121. Engine oil having dithiocarbamate and aldehyde/epoxide for improved seal performance, sludge and deposit performance. U.S. Patent 6,121,211 (9/9/2000, CF Stachew, WD Abraham, JA Supp, JR Shanklin, GD Lamb).
122. Viton seal compatible dispersant and lubricating oil composition containing same. U.S. Patent 5,188,745 (2/23/93).
123. Dibasic acid lubricating oil dispersant and viton seal additives. U.S. Patent 4,663,064 (5/5/87, TE Nalesnik, CM Cusano).
124. Lubricating oil dispersant and viton seal additives. U.S. Patent 4,636,322 (1/13/87, TE Nalesnik).
125. Dispersant additives. U.S. Patent 6,127,322 (10/3/2000, RM Scott, RW Shaw).
126. Method for preparing engine seal compatible dispersant for lubricating oils comprising reacting hydrocarbyl substituted dicarboxylic compound with aminoguanidine or basic salt thereof. U.S. Patent 5,080,815 (1/14/92, DJ Fenoglio, PR Vettel, DW Eggerding).
127. Compositions for control of induction system deposits. U.S. Patent 5,679,116 (10/21/97, LJ Cunningham, DP Hollrah, AM Kulinowski).
128. Deposit control additives and fuel compositions containing the same. U.S. Patent 5,334,228 (8/2/94, H Ashjian, MP Miller, D-M Shen, MM Wu).
129. Additive formulation of fuels incorporating ester function products and a detergent-dispersant. U.S. Patent 5,433,755 (7/18/95, P Mulard, Y Labruyere, A Forestiere, R Bre-gent).
130. Gear and transmission lubricant compositions of improved sludge-dispersibility, fluids comprising the same. U.S. Patent 5,665,685 (9/9/97).
131. Automatic transmission fluids and additives thereof. U.S. Patent 5,441,656 (8/15/95, H Otani, RJ Hartley).
132. Hydraulic automatic transmission fluid with superior friction performance. U.S. Patent 4,253,977 (3/3/81, R O'Halloran).
133. Lubricating oil composition for automatic transmission. U.S. Patent 5,972,854 (10/26/99, T Ichihashi, H Igarashi, J Deshimaru, T Ikeda).
134. Automatic transmission fluid composition. U.S. Patent (9/28/99, M Kitanaka).
135. Automatic transmission fluids having enhanced performance capabilities. U.S. Patent 5,972,851 (10/26/99, S Srinivasan, DW Smith, JP Sunne).
136. Gear oil additive concentrates and lubricants containing them. U.S. Patent 6,096,691 (8/1/2000, GS Conary, RJ Hartley).
137. Lubricating oil composition for high-speed gears. U.S. Patent 5,756,429 (5/26/98 Ichihashi, Toshihiko).
138. Hydraulic Fluids. U.S. Patent 5,767,045 (6/16/88, HT Ryan).
139. Use of dispersant additives as process antifoulants. U.S. Patent 5,368,777 (11/29/94, DR Forester).
140. Multifunctional antifoulant compositions. U.S. Patent 4,927,561 (5/22/90, DR Forester).
141. Multifunctional antifoulant compositions and methods of use thereof. U.S. Patent 4,775,458 (10/4/88, DR Forester).

Selection and Application of Solid Lubricants as Friction Modifiers

GINO MARIANI

Acheson Colloids Company, Port Huron, Michigan, U.S.A.

1 INTRODUCTION

Solid lubricants are considered to be any solid material that reduces the friction and mechanical interactions between surfaces in relative motion against the action of a load. Solid lubricants offer alternatives to the lubricant formulator for situations where traditional liquid additives fall short on performance. An example is a high-temperature lubrication condition in which oxidation and decomposition of the liquid lubricant will certainly occur, resulting in lubrication failure. Another example is for situations that generate high loads and contact stresses on bearing points of mating surfaces, producing a squeeze-out of the liquid lubricant and a resulting lubricant starvation (see [Figure 1](#)).

Solid lubricants, used as a dry film or as an additive in a liquid, provide enhanced lubrication for many different types of applications. Typical hot-temperature applications include oven chain lubrication and metal-deformation processes such as hot forging. Solid lubricants are also helpful for ambient temperature applications such as drawing and stamping of sheet metal or bar stock. Solid lubricants are effectively used in antiseize compounds and threading compounds, which provide a sealing function and a friction reduction effect for threaded pipe assembly [1]. Applications involving low sliding speeds and high contact loads, such as for gear lubrication, also benefit from solid lubricants. The solid lubricant effectively provides the required wear protection and load-bearing performance necessary from gear oil, especially capable when used with lower-viscosity base oils.

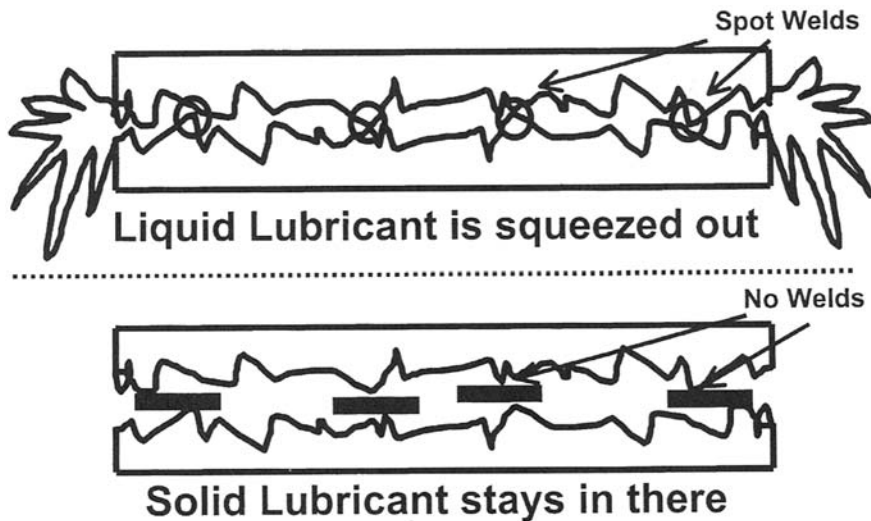


Figure 1 Contact stresses on bearing points of mating surfaces cause a squeeze-out.

Solid lubricants also assist applications where the sliding surfaces are of a “rough” texture or surface topography. Under this circumstance, the solid lubricant is more capable than liquid lubricants for covering the surface asperity of the mating surfaces. A typical application is a reciprocating motion that requires lubrication to minimize wear. Another application for solid lubricants is for cases where chemically active lubricant additives have not been found for a particular surface, such as polymers or ceramics. In this case, a solid lubricant would function to provide the necessary protection to the mating surfaces that would normally occur from the reaction of a liquid component to the surface [2].

Graphite and molybdenum disulfide (MoS_2) are the predominant materials used as a solid lubricant. These pigments are effective load-bearing lubricant additives due to their lamellar structure. Because of the solid and crystalline nature of these pigments, graphite and MoS_2 exhibit favorable tolerance to high-temperature and oxidizing atmosphere environments, whereas liquid lubricants typically will not survive. This characteristic makes graphite and molybdenum disulfide lubricants necessary for processes involving extreme temperatures or extreme contact pressures.

Other compounds that are useful solid lubricants include boron nitride, polytetrafluoroethylene (PTFE), talc, calcium fluoride, cerium fluoride, and tungsten disulfide. Any one of the compounds may be more suitable than graphite or MoS_2 for specific applications. Boron nitride and PTFE are discussed along with graphite and molybdenum disulfide in this chapter.

What are the basic requirements for an effective solid lubricant? Five properties must be met in a favorable way [3].

1. **Yield strength:** this refers to the force required to break through the lubricant or deform its film. There should be high yield strength to forces applied perpendicular to the lubricant. This will provide the required boundary lubrication and protection to loads between the mating surfaces.

Low yield strength of the film should be present in the direction of sliding in order to provide reduced coefficient of friction. This dependency on directional application of forces is considered an anisotropic property.

2. Adhesion to substrate: the lubricant must be formulated in a manner that maintains the lubricant film on the substrate for a sufficient period necessary for the lubrication requirements. The force of adhesion should exceed that of the shear forces applied to the film. Any premature adhesion failure will result in a nonprotective condition between the two sliding surfaces that require lubrication.
3. Cohesion: individual particles in the film of solid lubricant should be capable of building a thick enough layer to protect the high asperities of the surface and to provide a “reservoir” of lubricant for replenishment during consumption of the solid film (see Figures 2 and 3).
4. Orientation: the particles used must be oriented in a manner that parallels the flow of the stress forces and provide the maximum opportunity for a reduction in the coefficient of friction. For this to occur, it is necessary for the dimensions of the particles to be greatest in the direction of low shear.
5. Plastic flow: the lubricant should not undergo plastic deformation when loads are applied directly perpendicular to the direction of motion. The solid should be able to withstand the intimate contact between the mating surfaces so that a continuous film of lubrication is maintained.

This chapter attempts to guide the formulator toward making successful choices in solid lubricants. It briefly summarizes the physical and chemical properties of the solid lubricant and discusses the merits of each type of major lubricant as well as the recommended application. The information will assist in understanding the chemistry of the lubricant and its general mechanism of lubrication.

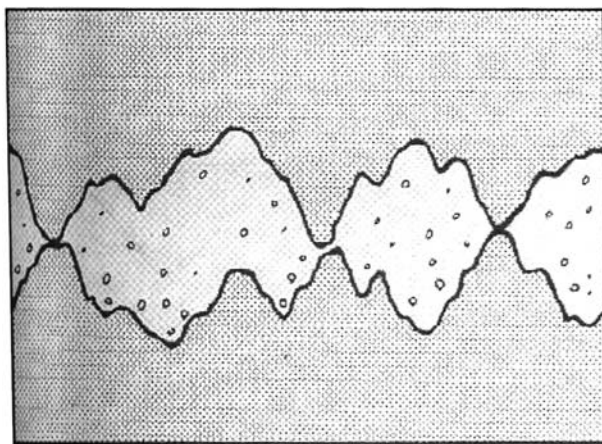


Figure 2 Surface asperities.

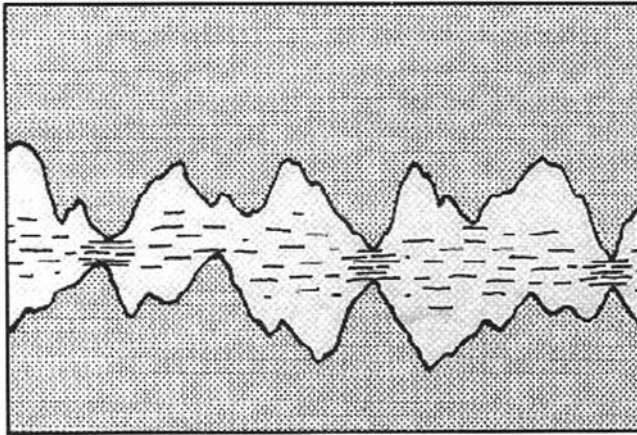


Figure 3 Burnished lubricant.

2 SOLID LUBRICANT PROPERTIES

2.1 Graphite

Graphite is most effective for applications involving high-temperature and high load-carrying situations. These capabilities make graphite the solid lubricant of choice for forging processes. Solid lubricants such as MoS_2 will oxidize too rapidly to be of any value at the typical hot-forging temperature range of 760°C to 1200°C , even though MoS_2 has a greater lubrication capability than graphite.

Why is graphite such a good lubricant? The answer lies in the platelet, lamellar structure of the graphite crystallite (see Figure 4). Graphite is structurally composed of planes of polycyclic carbon atoms that are hexagonal in orientation. Short bond lengths between each carbon atom within the plane are the result of strong covalent bonds (see Figure 4).

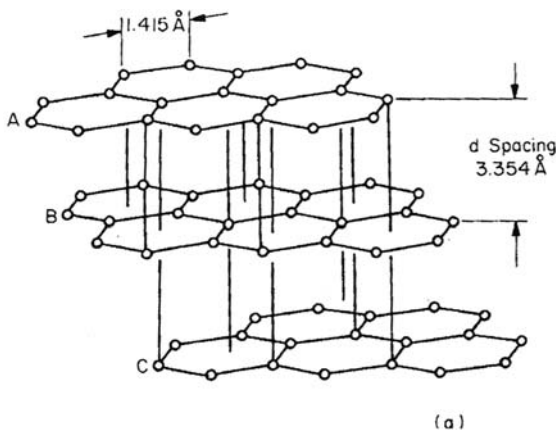


Figure 4 Structure of graphite.

Weaker van der Waal forces hold together a number of the planes to create the lattice structure. The d -spacing bond distance of carbon atoms between planes is longer and, therefore, weaker than the bond distance between carbon atoms within the planes. As a force is applied perpendicular to the crystallite, a strong resistance is applied against the force. This high yield strength provides the load-carrying capacity for the lubricant. Concurrent with the force applied perpendicular to the substrate is a sliding force applied parallel to the direction of sliding. The weak bond between the planes allows for easy shearing of the planes in the direction of the force. This creates a cleaving of the planes and results in friction reduction. The lamellar motion of graphite cleavage can be illustrated by the concept of a hand applying a force on a deck of playing cards as shown in Figure 5. Forces applied perpendicular to the deck are resisted by stack's thickness and yield strength. Yet a far easier force is required to rupture the stack when the force is applied parallel along the face of the deck, resulting in the shearing of the cards.

The effects of the lamellar structure of graphite can be observed when sliding conditions are applied onto metal surfaces. Coefficient-of-friction data can be generated by various bench test methods for measuring the lubricity of sliding conditions. In comparison to unlubricated or oil-lubricated metal surfaces, graphite provides excellent lubricity [4]. This is illustrated in [Table 1](#).

2.1.1 Sources of Graphite

There are many types and sources of graphite. These sources influence the properties of the graphite, which affects the performance of the end product that uses the graphite. Graphite is characterized by two main groupings: natural and synthetic.

Natural graphite is derived from mining operations worldwide. The ore is processed to recover the usable graphite. Varying quality of the graphite will be evident

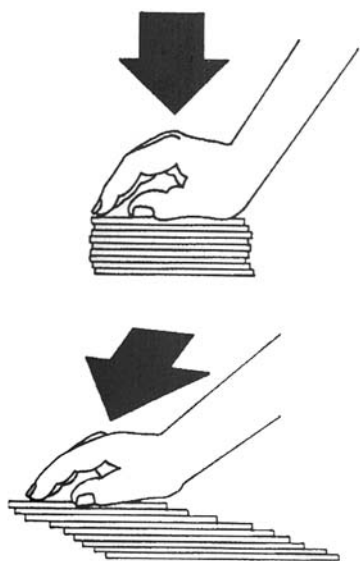


Figure 5 Representation of lamellar lubrication.

Table 1 Coefficients of Friction Provided by Graphite Films

Test method	Graphite film	Unlubricated metal	Mineral oil on metal
Three-ball slider	0.09–0.12	0.16–0.18	0.15–0.17
Bowden–Leben machine	0.07–0.10	0.40	0.17–0.22

as a result of the ore quality and postmining processing of the ore. High-purity natural graphite will normally be highly lubricating and resistant to oxidation. This is due to the high degree of crystal structure and graphitization usually associated with naturally derived graphite.

Natural graphite of lesser quality is also available. A lower total carbon content and a lower degree of graphitization characterize the lesser quality. The end product is graphite that is more amorphous in nature, with a higher content of ash components, which are mostly oxides of silicon and iron. Lubrication functionality decreases as crystallinity and graphitization decrease. Lubrication functionality also decreases as total ash content of the graphite increases.

Commercially available natural graphite is provided in a variety of grades. The suitability of the grades depends on the intended application and economic constraints. Table 2 characterizes examples of commercially available natural graphite.

Selecting the type of natural graphite to use is based on the degree of lubrication required for the application, the particle size of the graphite necessary for the application, and the economic constraint. For situations where the lubrication demand is severe, a high-carbon crystalline flake or crystalline vein graphite will be desired. The high degree of crystallinity and graphitization provides superior lubrication. A more economical alternative is the lower-carbon-content flake graphite. For most situations, those types of graphite perform adequately in lubricating conditions that do not require the purity and lubricity of higher-quality crystalline graphite. For occasions where only minor lubricity is needed and perhaps a more thermally insulating coating is required, then amorphous graphite would be chosen. Amorphous graphite is also the least expensive of the commercially available natural graphite grades. Combining amorphous and crystalline graphite can also be done to modify the amount of lubrication to suit the requirements of the application.

Synthetic graphite is an alternative source for lubricating graphite. Synthetic graphite is characterized as primary grade or secondary grade (see Table 3). Primary grade is derived synthetically from production within an electric furnace, utilizing

Table 2 Natural Graphite

	Amorphous	Crystalline flake 1	Crystalline flake 2	Crystalline vein
% Carbon	80.0	91.1	96.2	98.0
% Sulfur	0.25	0.18	0.11	0.74
% SiO ₂	6.65	0.30	0.07	0.18
% Ash	12.0	8.0	3.65	2.0
Mesh	–325	–325	–325	–325

Source: Ref. 5.

Table 3 Synthetic Graphite

	Primary	Primary	Secondary	Secondary
% Carbon	99.9	99.9	99.9	99.5
% Sulfur	trace	trace	0.01	0.01
% SiO ₂	0.02	0.02	0.05	0.43
% Ash	0.1	0.1	0.1	0.06

Source: Ref. 6.

calcined petroleum coke as well as very high temperatures and pressures to produce the graphite. The result is usually a product of high purity and can approach the quality of natural graphite flake in terms of percent graphitization and lubrication capability.

Secondary synthetic graphite is derived from primary graphite that has been used for the fabrication of electrodes. This type of graphite is usually less lubricating than natural or primary grades of graphite because of its lesser degree of crystallinity and graphitization and the presence of binding agents and surface oxides that do not contribute to lubrication. Secondary synthetic graphite is perfectly capable of lubricating effectively for many applications that can afford a lesser degree of lubricity. The chief benefit in using secondary synthetic graphite is economics, with the secondary graphite costing significantly less than primary-grade synthetic graphite or high-purity natural graphite.

2.1.2 Lubrication

Appropriate-quality graphite is able to meet the five criteria for an effective solid lubricant. Graphite possesses the necessary yield strength for successful lubrication. It is able to adhere sufficiently to metal surfaces due to its affinity to metal and its packing within and above the microstructure of the surface. Graphite has a burnishing capacity desirable for lubrication mechanisms that require a “memory” effect. Proper orientation of graphite particles is achieved by the natural tendency for the graphite crystal to orient itself parallel to the substrate and in the direction of lowest shear. The anisotropic characteristic of graphite lends itself well to its lubricating capability and friction-reduction property. The planar orientation of the graphite particles on the substrate takes advantage of the anisotropic property. Proper orientation allow the lamellar functionality of graphite where easy shear is achieved along the crystal plane when sliding forces are put along the length of the particles. The high yield strength in graphite is maintained in the direction perpendicular to the direction of shear force, providing for the load-carrying capability.

Graphite is best suited for lubrication in a regular atmosphere. Water vapor is a necessary component for graphite lubrication. The role that adsorbed water vapor plays in the lubricating properties of graphite has been studied [7]. It is theorized that water vapor helps to reduce the surface energy of the graphite crystallite. The adsorption of a water monolayer onto the planar surface of the graphite likely reduces the bonding energy between the hexagonal planes of the graphite to a level that is lower than the adhesion energy between a substrate and the graphite crystal.

This allows for lamellar displacement of the graphite crystals when shear forces are applied to the graphite film. The result is a reduction of friction and corresponding lubrication. Because water vapor is a requirement for lubrication, graphite is usually not effective as a lubricant in a vacuum atmosphere.

The lubricating ability of graphite as a function of temperature is very good. Graphite is able to withstand continuous temperatures of up to 450°C in an oxidizing atmosphere and still provide effective lubrication. The oxidation stability of graphite depends on the quality of the graphite, the particle size, and the presence of any contaminants that might accelerate the oxidation. Graphite will also function at much higher temperatures on an intermittent basis. Peak oxidation temperatures are typically near 675°C. For these instances, modifying the composition of the graphite mixture may be necessary as a way to control its rate of oxidation.

The thermal conductivity of graphite is generally low. For example, primary-grade synthetic graphite has a conductivity of $\sim 1.3 \text{ W/mK}$ at 40°C. Amorphous graphite is even less conducting and is sometime considered for providing some degree of thermal insulation for specific applications.

Table 4 illustrates some basic properties of graphite and how they vary based on the derivation of the graphite.

2.2 Molybdenum Disulfide

Molybdenum disulfide is the second significant solid lubricant widely used in industry. It has been used since the early 19th century for lubrication applications. MoS_2 , also known as molybdenite, is a mined material found in thin veins within granite. Lubricating-grade MoS_2 is highly refined by various methods in order to achieve a purity suitable for lubricants [9]. This purity usually exceeds 98%. MoS_2 is commercially available in a variety of particle-size ranges. Table 5 lists basic properties for molybdenum disulfide. The low friction of MoS_2 is an intrinsic property related to its crystal structure, whereas graphite requires the adsorption of water to behave as an effective lubricant. Molybdenum disulfide achieves its lubricating ability with a mechanism similar to graphite. Just like graphite, MoS_2 has a hexagonal crystal lattice structure (see Figure 6).

Sandwiches of planar hexagonal Mo atoms are interspersed between two layers of sulfur atoms. Similar to graphite, the bond strength between the hexagonal planes between the sulfur atoms are weak van der Waal-type bonds as compared to the

Table 4 General Properties of Graphite

	Amorphous	Natural	Natural	Primary	Secondary
% Carbon	81.0	90.0	96.7	99.9	99.7
% Graphite	28.0	99.9	99.9	99.9	92.3
Crystal size Å	>500	>1000	>1000	>1000	>700
<i>d</i> -spacing Å	3.361	3.355	3.354	3.355	3.359
Resistivity (ohm-cm)	0.091	0.031	0.029	0.035	0.042
Color	black	black	black	black	black
Specific gravity	2.31	2.29	2.26	2.25	2.24

Source: Ref. 8.

Table 5 Molybdenum Disulfide Characteristics

Property	Value
Molecular weight	160.08
Color	blue-gray to black
Luster	metallic
Specific gravity	4.80–5.0
Bulk hardness	1.0–1.5 Mohs
Melting point	>1800°C
Electrical conductivity	semiconductor
Thermal conductivity	0.13 W/mK @ 40°C
Crystal structure	hexagonal
Service temperature	up to 700°F
Coefficient of friction	0.10–0.15

Source: Ref. 10.

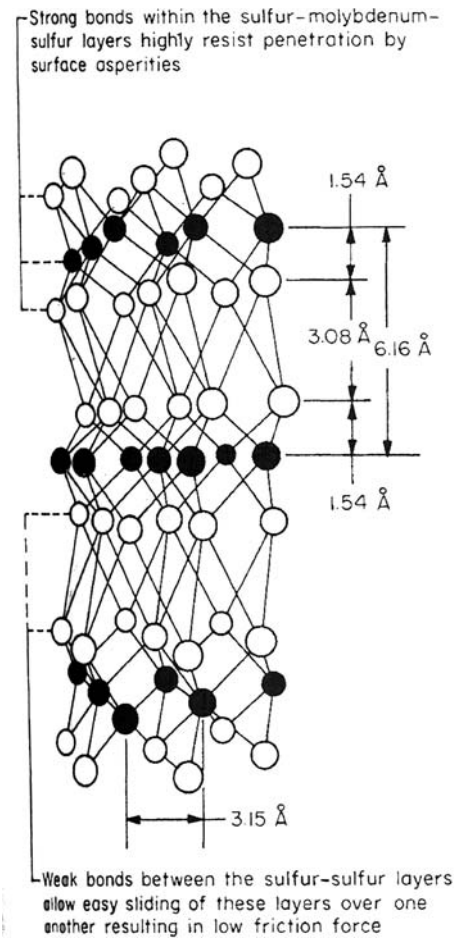


Figure 6 Lattice structure of molybdenum disulfide. (From Ref. 4, P 77.)

strong covalent bond between molybdenum and sulfur atoms within the hexagonal crystal. Orientation of the MoS_2 crystallites is important if effective friction reduction is to be achieved. MoS_2 has anisotropic properties that are comparable to graphite. When a force is applied parallel along the hexagonal planes, the weak bond strengths between the planes allow for easy shearing of the crystal, resulting in a lamellar mechanism of lubrication. At the same time, the crystal structure and strong interplanar bond forces of MoS_2 allow for high load-carrying against forces applied perpendicular to the plane of the crystal. This is necessary for the prevention of metal on metal contact for high-load applications such as gearbox lubrication.

MoS_2 scores well in the other criteria for an effective solid lubricant. It forms a strong cohesive film that is smoother than the surface of the substrate on which it is bonded. MoS_2 film has sufficiently high adhesion to most metal substrates that it successfully burnishes onto the wearing surfaces, thus minimizing metal wear and prolonging friction reduction. This characteristic is an exception, however, with titanium and aluminium substrates due to the presence of an oxide layer on the metal surface, which tends to reduce the tenacity of the MoS_2 film.

MoS_2 's lubrication performance often exceeds that of graphite. It is most effective for high load-carrying lubrication when temperatures are below 400°C . Another advantage of MoS_2 is that it lubricates in dry, vacuum-type environments, whereas graphite does not. This is due to the intrinsic lubrication property of MoS_2 . On the other hand, the lubricating ability of MoS_2 deteriorates in the presence of moisture because of oxidation of the MoS_2 into MoO_3 . The temperature limitation of MoS_2 is due to similar decomposition issues of the material as that experienced with moisture. As MoS_2 continues to oxidize, MoO_3 content increases, which induces abrasive behavior and an increasing coefficient of friction for the surfaces to be lubricated.

The effectiveness of MoS_2 improves as contact forces increase on the lubricated surface. Burnished surfaces exhibit coefficient-of-friction reduction as a function of increasing contact forces [11]. In contrast, graphite does not necessarily exhibit this behavior. The frictional property of MoS_2 systems has been reported to be generally better than graphite in many instances, up to the service-temperature limitations for the lubricant.

The particle size and film thickness of MoS_2 will affect lubrication. Generally, the particle size should be matched to the surface roughness of the substrate and the type of lubrication process considered. Too large a particle distribution may result in excessive wear and film reduction as mechanical abrasion is experienced. Too fine a particle size may result in accelerated oxidation in normal atmospheres as the high surface area of the particles promotes the rate of oxidation.

2.3 Boron Nitride

Boron nitride is a ceramic lubricant with interesting and unique properties. Its use as a solid lubricant is typically for niche applications when performance expectations render graphite or molybdenum disulfide unacceptable. The most interesting lubricant feature of boron nitride is its high-temperature resistance. Boron nitride's service temperature of 1200°C in an oxidizing atmosphere makes it desirable for applications that require lubrication at very high service temperatures. Graphite and molybdenum disulfide cannot approach that high of a service temperature and still remain intact. Boron nitride also has a high thermal conductivity property,

making it an excellent choice for lubricant applications that require rapid heat removal.

A reaction process generates boron nitride. Boric oxide and urea are reacted at temperatures from 800°C to 2000°C to create the ceramic material. Two chemical structures are available: cubic and hexagonal boron nitride. As one might expect, the hexagonal boron nitride is the lubricating version. Cubic boron nitride is a very hard substance used as an abrasive and cutting tool component. Cubic boron nitride does not have any lubrication value. The hexagonal version of boron nitride is analogous to graphite and molybdenum disulfide. The structure consists of hexagonal rings of boron and nitrogen that are connected to each other, forming a stack of planar hexagonal rings (see Figure 7). As with graphite, boron nitride exhibits a platelet structure (see Figure 8).

The bond strength within the rings is strong. The planes are stacked and held together by weaker bond forces. Similarly to graphite and molybdenum disulfide, this allows for easy shearing of the planes when a force is applied parallel to the plane. The ease of shear provides the expected friction reduction and resulting lubrication. Concurrently, the high bond strength between boron and nitrogen within the hexagonal rings provide the high load-carrying capability that is necessary to maintain metal-metal separation of the substrates. Similar to MoS_2 , boron nitride has intrinsic lubrication properties. Boron nitride effectively lubricates in a dry as well as a wet atmosphere. It is very resistant to oxidation, more so than either graphite or MoS_2 , and maintains its lubricating properties up to its service-temperature limit.

Commercial grades are available in a variety of purities and particle sizes. These varieties influence the degree of lubrication provided by boron nitride since particle size affects the degree of adhesion to substrate, burnishing ability, and particle orientation within a substrate. Impurities such as boric oxide content need to be considered with respect to the lubrication capability of boron nitride powder since this will influence the ability of the powder to reduce the coefficient of friction for

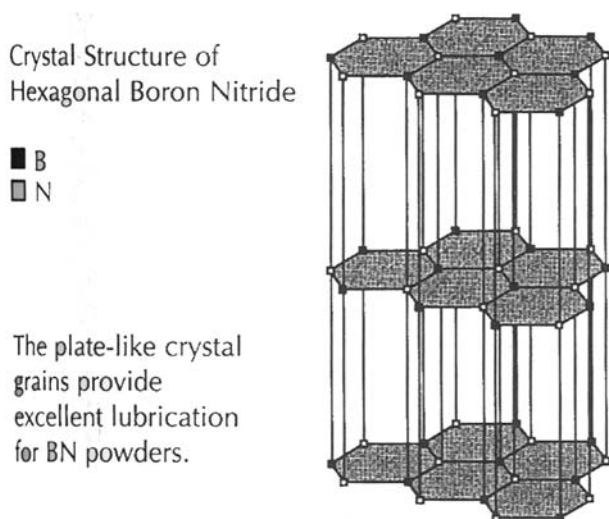


Figure 7 Crystal structure of hexagonal boron nitride.

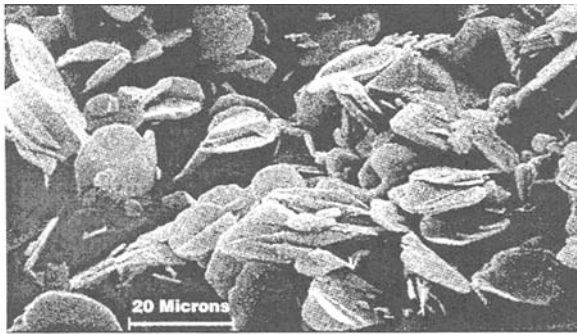
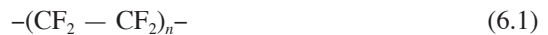


Figure 8 Scanning electron micrograph of boron nitride platelets. (From Ref. 13.)

an application. The variation in grades will also influence the thermal conductivity properties and ease of suspension in a liquid carrier. Table 6 summarizes typical properties for hexagonal boron nitride.

2.4 PTFE

PTFE is an acronym for polytetrafluoroethylene. PTFE has been in use as a lubricant since the early 1940s. Structurally, the polymer is a repeating chain of substituted ethylene with four fluorine atoms on each ethylene unit:



Contrary to the other lubricants discussed, PTFE does not have a layered lattice structure (see [Figure 9](#)). The lubrication properties are at least partially the result of its high softening point. As frictional heat begins to increase from sliding contact, the polymer maintains its durability and is able to lubricate.

Various grades are produced and applied to specific applications as a result of the properties imparted by the grade. For example, molecular weight and particle size are two characteristics that can alter performance of the polymer as a lubricant.

Table 6 Hexagonal Boron Nitride

Property	Value
Molecular weight	24.83
Density	2.27 g/cm ³
Crystal structure	hexagonal
Color	white
Dielectric strength	35 KV/mm
Dielectric constant	4.2
Thermal conductivity	55 W/mK
Coefficient of friction	0.2–0.7
Service temperature	1200°C (oxidizing atmosphere)
Practice size	1–10 micron grades

Source: Ref. 13.

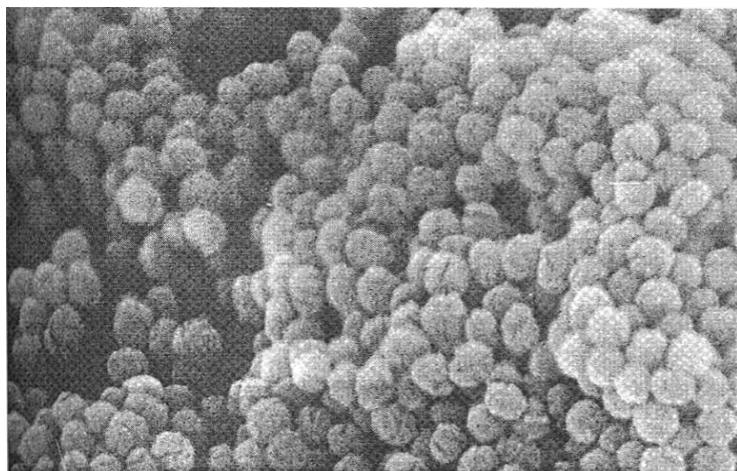


Figure 9 PTFE granules.

The critical characteristic of PTFE—one it is widely known for [14]—is the outstandingly low coefficient of friction imparted by the molecule. PTFE has one of the smallest coefficients of static and dynamic friction than any other solid lubricant. Values as low as 0.04 for sliding conditions have been reported for various combinations of PTFE films on substrates [15]. The low-friction property is attributed to the smooth molecular profile of the polymer chains, which orient in a manner that facilitates easy sliding and slip. It is postulated that the PTFE polymer results in rod-shaped macromolecules that can slip along each other, similar to lamellar structures. Its chemical inertness makes it useful in cryogenic to moderate operating temperatures, and in a variety of atmospheres and environments. Operating temperatures are limited to about 260°C due to decomposition of the polymer.

One consideration in using PTFE is the cold weld property of the material. This could eliminate its use for some applications where extreme pressure is encountered. Such pressure may result in the destruction of the polymer particle and result in lubrication failure as the PTFE congeals and fails to remain intact on the rubbing surface.

PTFE finds many uses in bonded film lubrication at ambient temperature. These applications include fasteners, threading compounds, and chain lubrication and engine oil treatments. PTFE is widely used as an additive in lubricating greases and oils, both for industrial and consumer applications (see [Table 7](#) for basic properties).

Although difficult to accomplish due to the low surface energy of PTFE, colloidal dispersions of PTFE in oil or water can be produced. This is useful for applications requiring the stable suspension of PTFE particles in the lubricating medium, such as for crankcase oil or hydraulic oil. The nature and feedstock of the PTFE influence the ability to create a stable, unflocculated dispersion that is necessary for effective lubrication.

Table 7 Physical Properties of PTFE

Property	Value
Specific gravity	2.13–2.22
Hardness	0.1 Shore D
Melting point	327°C
Coefficient of friction (ASTM D1894)	0.1
Dielectric constant	2.1
Service temperature	Up to 260°C

Source: Ref. 16.

3 PREPARATION FOR LUBRICANT APPLICATION

In order for a lubricant to be effective, the solid has to be applied in a manner that provides an effective interface between the mating substrates that require wear protection or lubrication. Dry-powder lubrication can be used, but it is limited in its scope of application. Simply put, the dry powder can be “sprinkled” onto the load-bearing substrate. By a combination of the rubbing action from sliding and the natural adhesion properties of the solid lubricant, some measure of attachment to the substrate will occur by burnishing to provide lubricating protection [17]. MoS₂ seems to function particularly well from this manner of application, as it appears to have an effective burnishing capability.

The use of free powder has limitations. The films tend to have a short duration of service since adhesion is usually insufficient to provide any longevity for a continuous application. The use of dry powder also makes it difficult in many circumstances to accurately apply the lubricant to the place intended, with the possible exception of tumbling metal billets for achieving a coating over phosphated substrates.

This can be overcome by the use of bonded films. Bonded films will provide a strong adhesion to the substrate requiring protection. It also allows for a more controlled rate of film wear, which depends on the properties of the bonding agent and the film thickness of the bonded film. Bonded films can be achieved by a number of ways, all by use of secondary additives that promote a durable and longer-lasting film. The intended application will dictate the appropriate type of bonding agent. For applications of continual service, resin and polymer bonding agents are typically used. These include phenolic resins, acrylics, celluloses, epoxies, polyimides, and silicons. Some of the binders such as epoxies are curable at room temperatures. Others such as the phenolic resins require elevated-temperature curing. Service temperature may be the limiting consideration for the chosen bonding agent.

To overcome service-temperature limitations, alternative type bonding agents are also widely used. Most typical are inorganic salts such as alkali silicates, borates, and phosphates. These types of salts overcome temperature limitations of organic bonding agents, transferring the burden of temperature consideration to the solid lubricant. Conversely, the use of inorganic salts as bonding agents typically does not provide for a coating life that is as durable as an organic bonded coating. This usually limits the application to those requiring constant replenishment of the lubricant.

To facilitate the application of the solid lubricant, dispersion in a liquid is most commonly used. The liquid can be a solvent, oil, synthetic oil, or water. Suspension within a liquid allows for the easy and precise application of the solid lubricant to the intended areas that require protection. Compared to dry-powder application, film control is easily achieved through spray, dip, or flow methods onto the substrate. Environmental cleanliness is also improved since the solid particles are entrapped within a liquid matrix, preventing the airborne dispersion of the particles. For applications for which the solid lubricant is a secondary additive in a liquid, proper suspension is critical for achieving effective lubrication.

A consideration for liquid suspensions is that shelf life of the lubricant is limited. Because the particles require suspension within a liquid carrier, eventual sedimentation of the solid lubricant will occur. This necessitates proper mixing procedures for the handling of the suspension in order to provide for consistent lubricant performance within the stated shelf life of the material. Adjustment to formulations with respect to dispersion and viscosity controls will influence the time it takes for the suspension to destabilize. The quality of the suspension will also determine how easily the settled pigment is redispersed with mild agitation (see Figure 10).

To create the suspension, the solid lubricant particles require treatment of the particle surface to make it amenable to suspension within the carrier liquid. This is similar to paint, where the colorant is chemically treated to provide the required dispersion characteristics and to form what is considered a colloidal suspension (see Figure 11). This treatment is necessary to maximize the available particles for lubrication and to provide the degree of dispersion stability required for the job. Without such treatment, particle agglomeration and rapid sedimentation will occur. This would negatively influence the application of the lubricant onto the substrate in a manner that creates an inferior and ineffective film. Wetting agents and suspending agents such as polymeric salts, starches, and polyacrylics are used to treat the surface of the solid lubricant to render it capable of suspension within the liquid carrier.

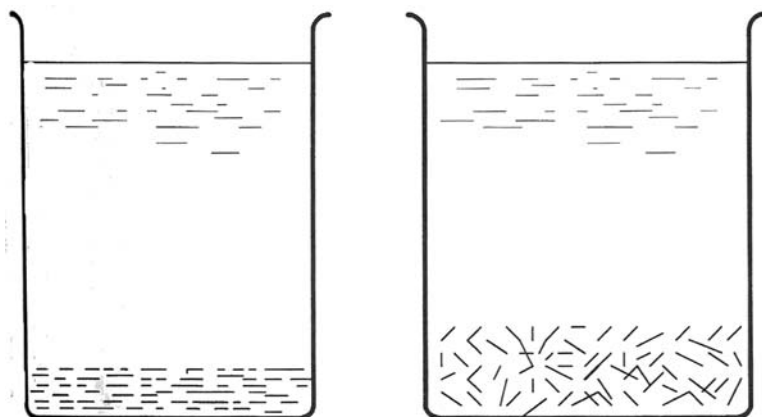


Figure 10 Particle sedimentation.

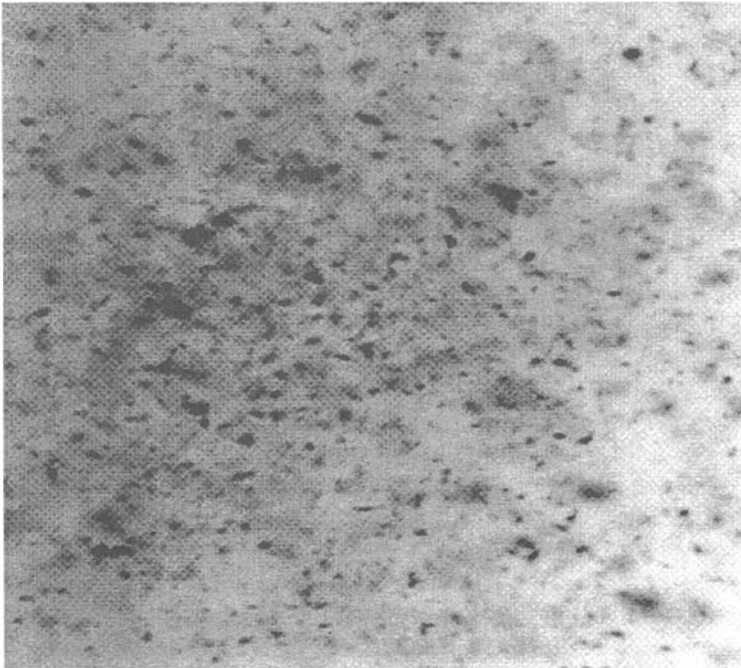


Figure 11 Colloidal dispersion.

When creating the dispersion, the particle-size distribution of the solid lubricant has to be considered. Small, submicron particles are easier to suspend and retain physical stability than large, coarse particles. To this end, milling action on the solid lubricant is usually necessary to alter the size distribution to the desired range of sizes (see [Figure 12](#)).

Fine-sized particles are not necessarily the best distribution for a particular lubricating application (see [Figure 13](#)). Some consideration is required for the most beneficial particle size to match up with the surface roughness and nature of the application. This consideration could run contrary to what is the best particle size for dispersion stability. Therefore, some degree of compromise may be necessary to achieve a balance of dispersion stability and lubrication performance.

Some type of substrate preparation for the load-bearing surface may be required to facilitate the application of the solid lubricant. This is usually necessary for metal-deformation processes so that the film thickness, film uniformity, and durability of the applied lubricant onto a billet will be robust enough to lubricate. Typical treatments of the surface include phosphating, peening, and shot blasting, which are especially useful for powder-tumbling applications. With water-based dispersions, heating the substrate to some elevated temperature is often necessary to activate the bonding agents. Substrate heating serves a dual purpose: it facilitates the evaporation of the water carrier, and it also initiates the physical/chemical bonding of the film onto the substrate.

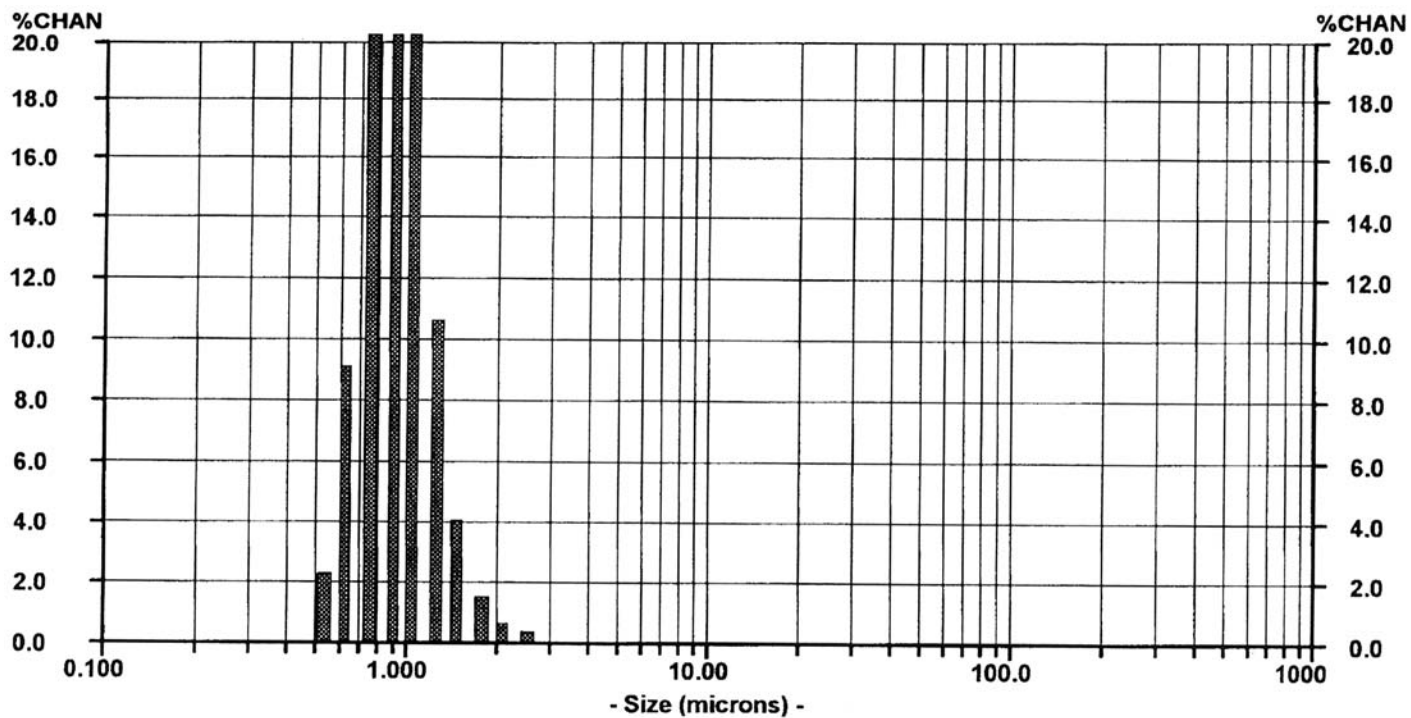


Figure 12 Particle-size distribution of colloidal graphite suspension.

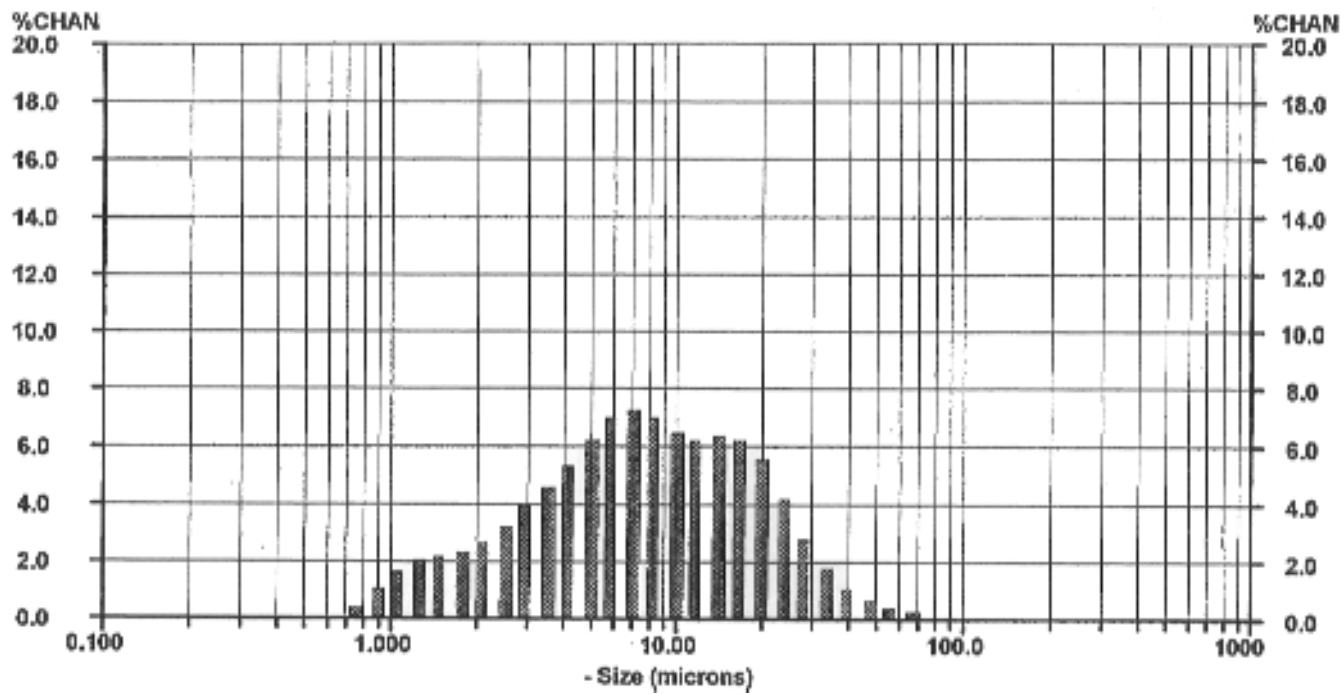


Figure 13 Coarse graphite particle-size distribution

4 APPLICATIONS

Two major lubrication applications are considered here: metal wear protection lubrication and lubrication for plastic deformation of metal. The former concerns applications such as constant sliding or reciprocating motion, for example gear, chain, or journal lubrication. The latter concerns applications where metal is under plastic flow, such as metal-forming or metal-cutting applications.

4.1 Wear Protection and General Lubrication

Wear protection and general lubrication applications are meant to include processes requiring hydrodynamic lubrication, elasto-hydrodynamic lubrication, and boundary lubrication. Examples of such applications include chain lubrication, gear lubrication, engine oil treatments, etc. In essence, any application where repetitive sliding or rolling contact occurs between two surfaces can be considered under the umbrella of wear protection lubrication. The intention is for the lubricant to reduce the coefficient of friction and protect against wear (see Figure 14). The benefits include savings in power consumption and service life of the component and efficiency gains due to the increased uptime resulting from proper lubrication.

Solid lubricants are useful and required for applications and conditions when conventional liquid lubricants are inadequate. These conditions would include

- High operating temperatures that eliminate or reduce the functionality of the liquid lubricant

- Contact pressure of sufficient magnitude that breaches the integrity of the liquid lubricant

- Performance enhancement that extends the capability of the conventional liquid lubricant

- Performance enhancement that extends the service life of the conventional liquid lubricant

- Applications that undergo a “start/stop” routine

- Applications that require low sliding speed but heavy bearing load

- Applications that require “fool-proofing” for potential catastrophic lubrication failures that result from lubricant starvation

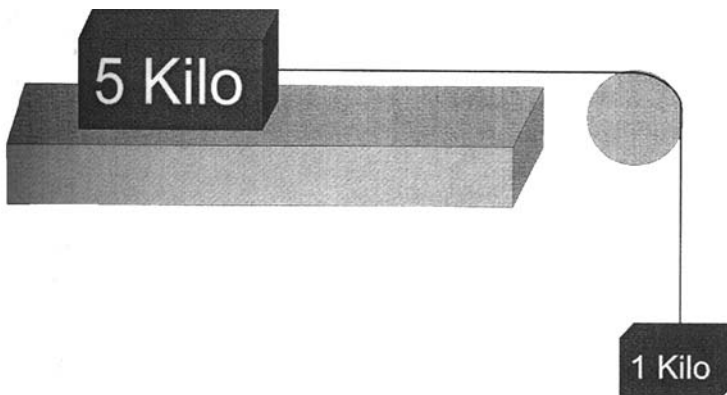


Figure 14 Lubrication of sliding surfaces-friction reduction.

For successful incorporation of a solid lubricant as a secondary additive into liquid lubricants, a well-formulated colloidal dispersion is required. As an example, consider a case study where gear oil performance is enhanced above that of a conventional liquid lubricant by use of colloidal solids. The addition of 1% colloidal molybdenum disulfide to an AGMA No. 7 and AGMA No. 8 gear oil reduced the break-in times and steady-state operating temperatures of low-viscosity synthetic oils as compared to nonfortified gear oils [18]. Table 8 summarizes a comparison of the performance of various blended gear oils to the measured output criteria as tested on a worm gear dynamometer.

Another example concerns the potential lubrication improvement from solid lubricants for friction-modified engine oils. Because of the burnishing property that solid lubricants such as colloidal graphite or colloidal MoS₂ would have on metal surfaces, friction reduction in engine and axle components might be expected. Along with friction reduction there should be a corresponding increase in fuel efficiency for motor vehicles. Various studies seem to support that conclusion. One report claims that in fleet trials conducted according to EPA 55/45 fuel economy testing with reference motor oils fortified with either MoS₂ or graphite, both in a colloidal dispersion, the fuel economy was improved by 4.5% [19]. In another fuel economy study using a fleet of taxicabs, the use of 2% colloidal graphite or colloidal MoS₂ in low-viscosity-formulated engine oils and rear-axle lubricants improved the fuel economy by 2.5% [20].

The friction-reducing influence of colloidal graphite in oil is illustrated in one study by a dynamometer evaluation conducted on a 2.3-liter engine (see Table 9). The study indicates that graphite properly dispersed in an appropriate liquid lubricant will considerably reduce friction with the subsequent benefit of fuel economy savings.

Solid lubricants are also applied as bonded films for certain applications. For example, applications requiring a permanent or semipermanent lubricating film would require a bonded film. Bonded coatings are commonly formulated with MoS₂ or PTFE. One example would be for self-lubricating composites that require high-temperature stability, such as for what may be needed for engine piston ring

Table 8 Worm Gear Dynamometer Tests

Description	Performance parameters output torque = 113 <i>N-m</i>		
	Mean input torque (<i>N-m</i>)	Percent efficiency	Mean oil sump temperature (°C)
AGMA #8 gear oil	6.02	62.6	92.1
AGMA #8 gear oil + 1% colloidal MoS ₂ dispersion	5.92	63.6	95.5
AGMA #7 gear oil	6.05	62.3	93.6
AGMA #7 gear oil + 1% colloidal MoS ₂ dispersion	5.89	64.0	93.4
Synthetic PAG #2 oil	6.09	61.8	108.8
Synthetic PAG #2 oil + 1% MoS ₂ dispersion	5.79	65.1	88.4

Source: Ref. 18.

Table 9 Liter Engine Dynamometer Study

Wt. % colloidal graphite	Cyclic test		Steady state*	
	Averaged fuel economy (mpg)	Improvement over baseline (%)	Averaged fuel economy (mpg)	Improvement over baseline (mpg)
none	16.91	baseline	17.50	baseline
0.5	17.31	2.4	17.59	0.5
1.0	17.77	5.1	18.03	3.0

Source: Ref. 21.

*Averaged for 40, 50, and 55 mph.

protection [22]. Other examples that benefit from a bonded lubricant include fasteners, chains, and reciprocating mechanisms that require a persistent lubricating film. For these applications, PTFE stands out due to its low coefficient-of-friction. This is illustrated in Table 10 by comparative coefficient-of-friction data for PTFE, graphite, and MoS₂ that are bonded onto cold-rolled steel substrates.

In assessing the lubrication potential for dispersed solid lubricants, some type of bench testing is utilized to characterize the apparent lubrication performance of the material. The most typical lubrication tests are Shell 4-Ball Wear method, Shell 4-Ball EP method, Falex Pin-Vee Method, Plint Reciprocating method, Incline Plane method, and FZG Gear Lubrication method. In many cases, custom lubrication tests are developed for the specific application to be considered. When conducting bench testing for lubricant performance, correlation is best achieved when the mode of contact and conditions of the application are closely replicated by the bench test (see Figure 15). The configuration of the contact points for the application is matched with a similar mode of contact for the bench test.

For an illustration of laboratory lubrication assessments, see Table 11 to compare the empirical performance of the four solid lubricants dispersed in an oil carrier. The lubricants were tested according to two common methods of lubrication evaluation.

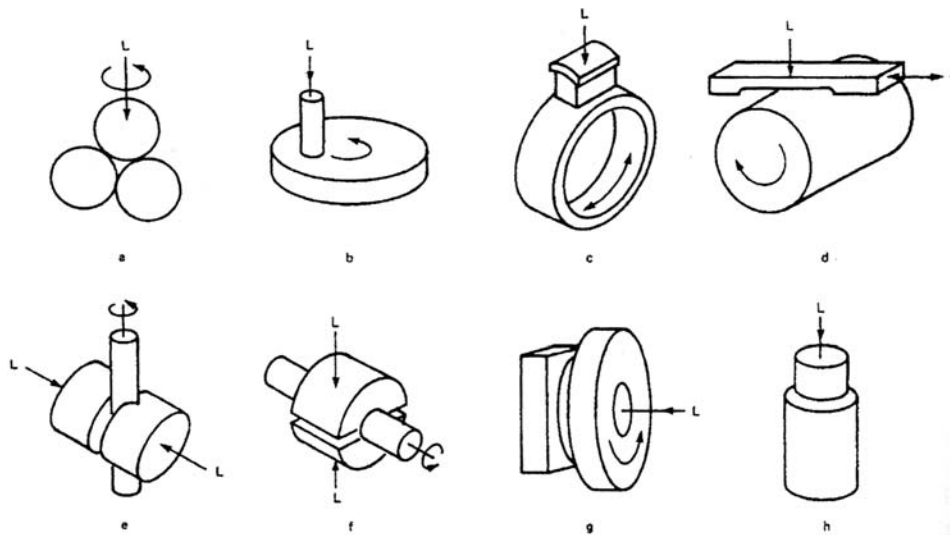
In this example, the dispersion of MoS₂ and PTFE provides effective load bearing, wear resistance, and coefficient-of-friction reduction when evaluated by a point-to-point contact (four ball) and line-to-point contact (Falex pin-vee). Interpretation of any bench test result must be done carefully to ensure the validity of extrapolating the test performance to the actual application.

Table 10 Coefficient of Friction for Bonded films

	Coefficient of friction*
MoS ₂	0.23
Graphite	0.15
PTFE	0.07

Source: Ref. 23.

*Evaluated at room temperature, ASTM D4918.



Wear-testing apparatus for solid lubricants. Initial point contact: (a) four-ball; (b) hemisphere on disc (may be 3 pins). **Initial line contact:** (c) block on ring (Timken, LFW1); (d) Reciprocating pad on ring; and (e) Falex. **Conforming contact:** (f) journal bearing (Almen-Wieland); (g) thrust bearing (LFW3); and (h) Press-fit (LFW4).

Figure 15 Wear-testing apparatus for solid lubricants.

What criteria should be considered for an application when selecting the preferred or optimal solid lubricant? First consider the service temperature for the application. This dictates what solid lubricant can be used. For example, MoS_2 generally has a higher load-carrying capability than graphite. Yet at service temperatures above 400°C , MoS_2 degrades and loses its lubricating capacity. MoS_2 is, therefore, eliminated from consideration if the service temperature is above 400°C .

The second consideration is environment. Atmospheric restrictions will eliminate the use of certain solid lubricants. For example, a vacuum environment will eliminate the use of graphite. As mentioned previously, graphite requires adsorption of water molecules to its surface in order to function effectively as a lubricant. MoS_2 , on the other hand, as well as PTFE and boron nitride, have intrinsic lubrication properties and do not require water molecules on their surface to provide friction-reduction value.

The third criterion is the nature of the lubricant; either a liquid fortified with solid lubricant additives or a bonded solid lubricant film. Some pigments are easier to disperse in liquid than others. For example, graphite and MoS_2 are comparatively easier to disperse in liquids than PTFE and boron nitride. This is due mostly to particle-size-reducing capability, surface energy, and surface chemistry of the solid lubricant.

The particle size of the pigment has an influence on lubrication performance. The size of the particulate and the size distribution of the particles should be optimized for the application (see Figure 16). For example, larger particles appear to give better performance for applications that are slow in speed or oscillating in nature.

Table 11 Bench Lubrication Test Results

	Four ball lubrication test				Falex lubrication test		
	Wear ASTM D-4172		Extreme pressure ASTM D-2783		Wear ASTM D-2670	EP ASTM D-3233	Coefficient of friction
	20 kg mm	40 kg mm	Weld (kg)	Load wear index (kg)	Teeth	lb to failure	Calculated
Base oil	0.678	1.060	126	17.20	fail	875	0.159
With 1% colloidal graphite	0.695	0.855	160	18.7	78	1000	0.132
With 1% colloidal MoS ₂	0.680	0.805	200	24.3	8	4375	0.077
With 1% colloidal PTFE	0.50	0.84	200	29.04	10	4500+	0.0568
With 1% colloidal BN	0.37	0.72	126	19.9	fail	500	0.1602

Source: Ref. 23.

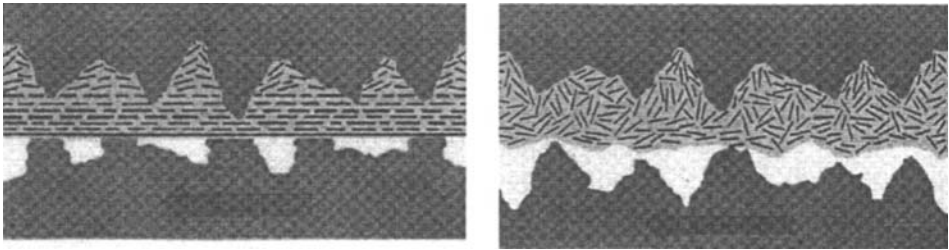


Figure 16 Orientation of solid lubricant particles in direction of motion.

Large particles also tend to give better performance on substrates where the surface roughness is relatively coarse.

A finer particle size tends to provide superior results for applications with constant motion and high speeds. Finer particles tend to function better where the surface roughness is relatively fine. Although not always predictable, the influence of particle size needs to be considered not only for dispersion requirements but also for the intended use application as well.

A fourth criterion involves cost-effectiveness of the lubricant. When the application conditions are met with two or more solid lubricants, economics will dictate the choice. Generally, graphite will be the least expensive in cost. High-purity graphite is more expensive than lower-purity natural graphite or secondary synthetic graphite, which are more expensive than low-quality graphite. Molybdenum disulfide will be next in cost, followed by PTFE and boron nitride as the more expensive solid lubricants. Cost-effectiveness for any of the solid lubricants will be influenced by the quality of the lubricant and formulation that utilizes the lubricant. The effectiveness of the final formulation may prove that a more costly solid lubricant is more cost-effective in use. [Table 12](#) attempts to rate the effectiveness of the solid lubricants for various criteria of application.

4.2 Lubrication for Plastic Deformation of Metals

Lubrication requirements for assisting metal-deformation operations such as forging (see [Figure 17](#)) and metal drawing are far more demanding than those for wear lubrication. The metal movement process creates very fast metal flow and rapid new surface generation. This creates a demand for a lubricant to flow with the metal, remain adhered to the surface, maintain sufficient film cohesion to “meter” out the lubricant with the advancing metal, and interact rapidly with the newly formed metal surface. Metal-forming operations are inherently high-load and high-stress processes, which put a significant demand on protective lubrication.

Most applications are conducted at an elevated temperature region. Under this circumstance, conventional liquid lubricants fail to withstand the stresses for the application. Solid lubricants are most appropriate for such applications because of their ability to withstand the operating temperatures, orient and adhere to the substrate surface, provide the coefficient-of-friction reduction necessary to promote metal flow, and provide the required load-carrying properties to prevent metal-on-metal contact. Indeed, most applications that involve plastic deformation of metal

Table 12 Solid Lubricant Selection Comparison and Rating

Criteria	Graphite	MoS ₂	PTFE	Boron nitride
Normal atmospheres	1	1	1	1
Vacuum atmospheres	3	1	1	1
Ambient temperature	1	1	1	1
Continuous service temperature to 260°C in air	1	1	1	1
Continuous service temperature to 400°C in air	1	3	N/A	1
Continuous service temperature to 450°C in air	2	3	N/A	1
Burnishing capability	1	1	3	2
Hydrolytic stability	1	2	1	1
Thermal conductivity	2	3	3	1
Load-carrying lubrication	2	1	1	2
Friction reduction	2	2	1	3
Dispersability	1	1	3	2
Color	black	gray	white	white
Relative cost	1	2	2	3

1 = best.

will utilize solid lubricants as either the primary or secondary lubricant within a formulation.

What application criteria are used used for determining the necessity for a solid lubricant? Severity of metal movement is the most significant factor. In cases where it is judged that metal movement would be considered extreme, solid lubricants will most likely be required. Application examples include forward, backward, and extreme lateral extrusion of metals. For example, forging of spindles, CV joints, crankshafts, and hubs would fall in this category. For these and similar cases, liquid lubricant technology falls short of providing the necessary lubrication, coefficient-of-friction reduction and die wear protection.



Figure 17 Forging press.

Once it has been determined that a solid lubricant is necessary, the temperature criteria need to be determined. Metal-working applications done at ambient temperature can utilize MoS_2 as the solid lubricant. MoS_2 has the best lubrication properties among the four lubricants discussed. In fact, for applications such as cold forging, MoS_2 is the preferred lubricant because of its ability to handle the very high load and stress applied onto the part being deformed.

In some cases, application of the MoS_2 is applied by dry-powder tumbling of the billets. Usually the billets are phosphated prior to applying powder in order to anchor the MoS_2 onto the surface and within the structure of the phosphate coating. The phosphate coating acts as an anchor for the powder and allows the lubricant to advance with the metal deformation. Table 13 compares forging performance for bare versus coated steel. Lubrication is improved as press tonnage falls and spike height of the forged billet increases.

Dry-powder tumbling is an effective application method for some cases. Other situations will require a more detailed and accurate depositing of MoS_2 film onto the substrate. This requires the use of a dispersed MoS_2 to provide a controlled coating thickness and particle-size distribution considered appropriate for the job.

There may be instances where MoS_2 is not desirable; for example, environmental concerns or housekeeping issues. In these instances, PTFE or boron nitride would be appropriate. The white color of the pigments alleviates concerns regarding cleanliness of using graphite and molybdenum disulfide. Situations that require a reduction in emissions and material reactivity would favor boron nitride since PTFE will decompose at typical warm and hot forging temperatures. Both would effectively lubricate, with perhaps boron nitride faring better than PTFE for applications with significant metal flow.

PTFE can, however, stand out as a lubricant for cold metal-forming operations involving sheet stock and bar stock. The low coefficient of friction imparted by PTFE will provide the necessary lubrication to assist metal flow in a manner far better than boron nitride and much cleaner than graphite or molybdenum disulfide.

All the solid lubricants would be appropriate for bonded-film applications for metal-deformation processes. Bonded films are desirable for sheetmetal applications where coil or blank metal is prepared with a dry-film lubricant. When developing bonded-film lubricants, consider the formulation of effective binders and bonding agents so that the solid lubricant can function as intended.

For metal-working applications at elevated temperatures, the operating temperature will determine which solid lubricant can be used. All the solid lubricants mentioned would be suitable for temperatures up to 260°C . Above that temperature, PTFE will be eliminated from consideration due to its decomposition. MoS_2 will be suitable for applications up to 400°C in an oxidizing environment. Above that

Table 13 Cold-Forging Lubrication

Sample	Press tonnage	Spike height (mm)
Bare steel	80.2	10.67
Bare steel + zinc phosphate	79.6	11.11
Bare steel + zinc phosphate + MoS_2	78.4	11.46

Source: Ref. 23.

temperature, decomposition of the MoS_2 will occur. Both graphite and boron nitride will lubricate effectively above the 400°C operating temperature. Graphite is the predominant lubricant used for plastic deformation at elevated temperatures.

The use of graphite is common and preferred for what is considered warm- and hot-forging situations. The forging process is considered warm forging when billet temperatures are up to 950°C . The process is considered hot forging when billet temperatures exceed 950°C . For both cases, oxidation of the graphite will occur. But the rate of oxidation depends on temperature and is regulated by formulation and graphite characteristics. Graphite quality, contaminants, crystallite size, and particle size will influence the rate of oxidation. The components of the finished formulation will also play a role in controlling the oxidation rate of the graphite, allowing it to survive the appropriate length of time necessary for lubricating the process.

The type and quality of graphite play an important role in performance. Its consideration is a first step in a selection process. The first choice is to choose between natural and synthetic graphite. Often the choice is dictated by the degree of graphite quality suitable for the application. For instances when average lubrication is required, natural graphite of lesser quality can be used. More demanding lubrication will require the use of high-purity synthetic or natural graphite.

Selection of the particle size of the graphite will vary depending on the intentions for the job. Particle size should be matched to the type of metal movement expected from the process, the surface roughness of the die and part, and the degree of stability required for the formulated lubricant. If a large particle distribution is desired, then concern about physical stability of the lubricant must be addressed. Rapid settling and hard packing of the graphite could occur due to the large particle size if countermeasures are not taken. This would create handling costs and product inconsistency for the end user.

For most circumstances, high-quality graphite should be used so that performance inconsistency is minimized. The quality and characteristic of the graphite can affect lubricating performance. Table 14 illustrates a lubricity comparison of standard formulations produced with different graphite. In this example, the application is warm forging of steel. Actual forging of a steel billet generates lubrication data where the spike height is determined using preset forging press parameters (see [Figure 18](#)). A longer spike height and lower coefficient of friction suggest better lubrication from the coating.

Once the type of graphite to be used is selected, then the cost of the powder needs to be considered versus the benefit derived from its use. In general, high-purity natural or primary synthetic graphite will be costlier than secondary synthetic

Table 14 Graphite Influence on Forging Lubrication (800°C Forging Temperature)

Graphite	Spike height (mm)	C.O.F.
A	1.5	0.05
B	1.3	0.08
C	1.1	0.10



Figure 18 Deformed billet and spike.

graphite. However, the performance benefit of using the higher-cost material may justify its selection for the application. Benefits normally associated with the higher-cost materials are consistency, lubricating performance, and reduced oxidation rates of the graphite.

The chosen graphite should be of a specific particle-size distribution in order to derive certain benefits in performance. These benefits include the ease of dispersing the graphite into a liquid carrier, the stability of the graphite within the concentrated product, the application and film formation of the product onto the workpiece, and the optimized lubrication for the deformation process.

Forging processes normally require a temporary bond of the lubricant onto the workpiece and tool. This is achieved by the use of the type of bonding agents mentioned previously in this chapter. The use of dry powder or simple liquid-powder mixes will not perform adequately because of the poor adhesion onto the substrate.

To illustrate the value of graphite for hot-temperature metal-working applications, consider the example cited in Table 15. A comparison is made between two formulated graphite products and a nongraphite product tested under the same procedures of warm forging. In this example, the degree of spike height and coefficient of friction generated by the forging process are determined. The lower spike height and higher coefficient of friction for the nongraphite lubricant are indications of reduced lubrication capability in comparison to the graphite-containing materials.

Table 15 Lubrication Comparison of Forging Lubricants (800°C Forging Temperature)

Lubricant	Spike height (mm)	C.O.F.
Graphite A	1.5	0.05
Graphite B	1.3	0.08
Nongraphite lubricant	0.7	0.15

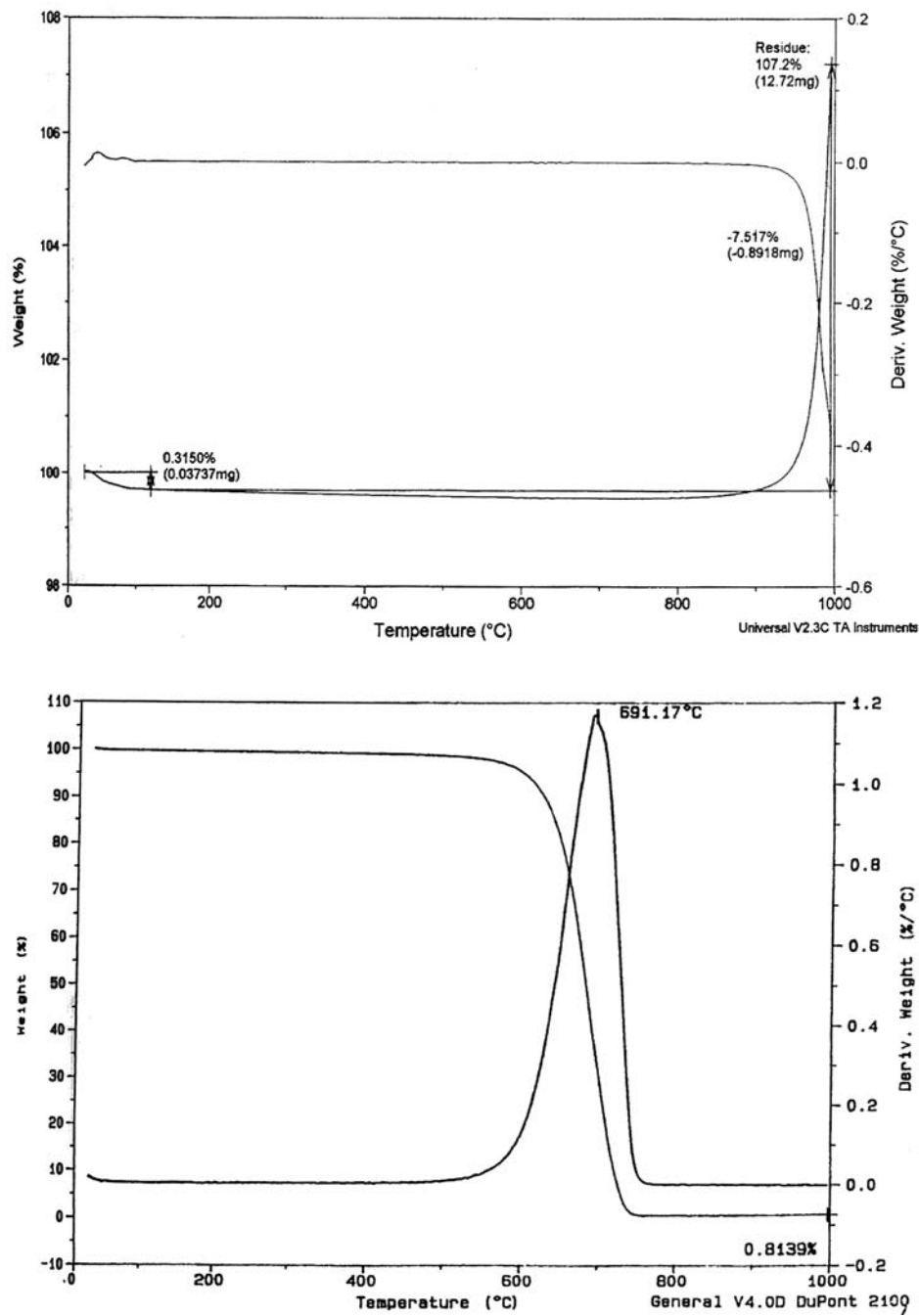


Figure 19 Comparison of peak oxidation temperature. (From Ref. 23.)

In certain instances, graphite is not desirable due to either the operating temperature or concern about housekeeping and cleanliness. Hexagonal boron nitride is a capable alternative to graphite for these conditions. It is considered the “white graphite” due to its lamellar structure. It has a reasonably low coefficient of friction, which approaches and sometime exceeds that of graphite. It is able to withstand operating temperatures up to 1200°C in oxidizing environments. This makes boron nitride an effective material for high-alloy isothermal forging, where extremely high temperatures and long contact times are encountered. A profile of oxidation characteristics provides a comparison of oxidation stability between boron nitride and graphite (see Figure 19). The ability for boron nitride to remain intact at very high temperature makes it ideal for applications that require a long residency time for the lubricant coating.

Another advantage to using boron nitride is the heat-conductivity property of the material. For applications that would require rapid heat dissipation, boron nitride serves quite well and is superior to graphite in that regard. Thermal conductivity values of boron nitride powder will vary depending on its quality. But boron nitride in any of its grades is invariably more thermally conductive than graphite or MoS₂. Applications such as high-performance cutting oils are claimed to deliver benefits of enhanced lubrication and heat withdrawal when finely dispersed submicron particles of boron nitride are incorporated into the fluid [25].

REFERENCES

1. U.S. Patent 5,180,509 (1/19/93, NL Jacobs).
2. KC Ludema. Friction, Wear, Lubrication, A Textbook in Tribology. Boca Raton, FL: CRC Press, 1996, p 123.
3. Acheson Colloids company, J. Brian Peace Lecture.
4. FJ Clauss. Solid Lubricants and Self-Lubricating Solids. New York: Academic Press, 1972, p 45.
5. Asbury Graphite product data sheets.
6. UCAR Graphite and Asbury Graphite product data sheets.
7. RH Savage. Graphite lubrication. J. Applied Physics 19:1, 1948.
8. WM Kenan. Characteristics of graphite lubricants. NLGI Spokesman 56(11), 1993.
9. HF Barry. Factors relating to the performance of MoS₂ as a lubricant. J Am Soc of Lubrication Eng 33(9):475–480, 1977.
10. Climax Molybdenum technical sheet.
11. AK Kohli, B Prakash. Contact pressure dependency in frictional behavior of burnished molybdenum disulphide coatings. Tribology Trans 44(1), 2001.
12. ZYP Coatings technical data sheet, Boron Nitride Powders for Research and Industry.
13. Advanced Ceramics technical data bulletin.
14. Du Pont Teflon® Fluoroaditives brochure.
15. FP Bowden, D Tabor. The Friction and Lubrication of Solids. New York: Oxford University Press, 1986, p 165.
16. Du Pont Teflon® Fluoroaditives brochure.
17. RG Kaur, CF Higgs, H Hesmat. Pin-on-disc tests of pelletized molybdenum disulfide. Tribology Trans 44:79–87, 2001.
18. PJ Pacholke, KM Marshak. Improved worm gear performance with colloidal molybdenum disulfide containing lubricants, ASLE paper presented at the 41st Annual Meeting in Toronto, Ontario, Canada, May 12–15, 1986.

19. ML Haviland, MC Goodwin. Fuel economy improvements with friction-modified engine oils in Environmental Protection Agency and road tests. Society of Automotive Engineers Technical Paper 790,945, Oct. 1979.
20. ML Haviland, JL Linden. Taxicab fuel economy and engine and rear axle durability with low viscosity and friction modified lubricants. Society of Automotive Engineers Technical Paper 821,227 Oct. 1982.
21. VE Broman et al. Testing of friction modified crankcase oils for improved fuel economy. Society of Automotive Engineers Technical Paper 780,597, June 1978.
22. U.S. Patent, 5,702,769 (12/30/97, JA Peters).
23. Acheson Colloids test data.
24. RE Booser. Theory and Practice of Tribology, Vol. II, Theory and Design. Boca Raton, FL: CRC Press, 1983, p 276.
25. U.S. Patent 5,985,802 (11/16/99, K Watari, HJ Huang, M Turiyama, A. Osuka, O. Yamamoto).

Organic Friction Modifiers

DICK KENBEEK and THOMAS F. BUENEMANN

Uniqema, Gouda, The Netherlands

1 INTRODUCTION

Friction modifiers of friction reducers have been applied for several years. Originally the application was for limited slip gear oils, automatic-transmission fluids, slideway lubricants, and multipurpose tractor fluids. Such products made use of friction modification to meet requirements for smooth transition from static to dynamic conditions as well as reduced noise, frictional heat, and startup torque.

Since fuel economy became an international issue, initially to reduce crude oil consumption, friction modifiers have been introduced into automotive crankcase lubricants as well, to improve fuel efficiency via the lubricant. In the United States, additional pressure is imposed on OEMs by the corporate average fuel economy (CAFE) regulation.

Following the introduction of vehicle exhaust emission regulations in various regions around the world, emphasis on friction reduction further increased. This can be well understood if it is realized that 20–25% of the energy generated in an engine by burning fuel is lost through friction [1]. The biggest part is lost by friction on the piston liner/piston ring interface, a smaller part by bearing and valve train friction. It is predicted that in future engines the contribution of the piston group to engine friction will increase up to 50% [2].

Reduction of fuel consumption and emissions can be achieved through [3]

Engine design changes and modifications, such as
 application of roller followers
 use of coatings
 surface modifications
 material selection

Fuel quality
The engine lubricant

All these aspects are looked at and/or applied in the automotive industry. This chapter concentrates on the engine lubricant.

The need to measure fuel savings has led to the development of API test Sequences such as VI and VIA in the United States. Sequence VIB will be used for ILSAC GF-3. In Europe a fuel economy test has been developed by CEC (test number CEC L-54-T-96) for the ACEA A1 and B1 specifications using the DBM 111 engine. Both tests require that the candidate lubricant show decreased fuel consumption relative to a reference oil.

2 FRICTION AND LUBRICATION REGIMES

Friction is defined as “the resistance a body meets while moving over another body in respect of transmitting motion.” The friction coefficient is defined as

$$F_w/F_n \quad (7.1)$$

where F_w is the frictional force and F_n the normal force or load.

For a lubricated surface, the coefficient of friction is determined by the lubrication regime. In simple terms, three lubricant regimes can be distinguished:

1. **(Elasto-)hydrodynamic regime (EHL)** characterized by a (relatively) thick lubricant film [4]. The mating surfaces are far enough apart to prevent metal-to-metal contact. The load on the system is fully carried by the lubricant film, and the viscosity of the lubricant determines the friction coefficient. Viscosity depends on temperature and pressure/viscosity coefficient.
2. **Boundary regime (BL)** characterized by a thin lubricant film [5]. Under high loads, high temperature, or with low viscosity oils, most of the lubricating film is squeezed out between the metal surfaces and metal-to-metal contact occurs. The load is entirely carried by the metal asperities. A thin layer of absorbed or otherwise deposited molecules is necessary to prevent the two surfaces and their asperities from plowing into each other.
3. **Mixed lubrication regime (ML)** characterized by a lubricant film of intermediate thickness [6]. The two metal surfaces have come closer together compared to hydrodynamic lubrication, and metal-to-metal contact occasionally occurs. The load is carried by both the lubricant and the asperities.

These regimes are related to the friction coefficient f by a lubricant parameter defined as

$$su/F \quad \text{or} \quad su/p \quad (7.2)$$

where

s = system speed.
 u = lubricant dynamic viscosity.

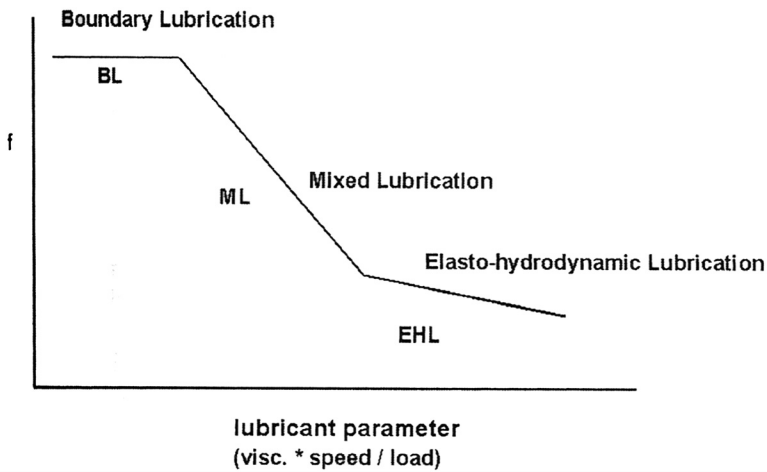


Figure 1 Stribeck curve at high contact pressure.

$F = \text{load } (F_n).$

$p = \text{contact pressure.}$

The so-called Stribeck curve gives the relationship between f and this lubricant parameter. The shape of the Stribeck curve and the transitions from BL to ML and ML to EHL depend on a number of parameters such as material roughness (micro-geometry), contact pressure, and lubricant viscosity. High contact pressure such as that present at point contacts leads to a different Stribeck curve as at line contact (lower contact pressure) (see Figures 1 and 2).

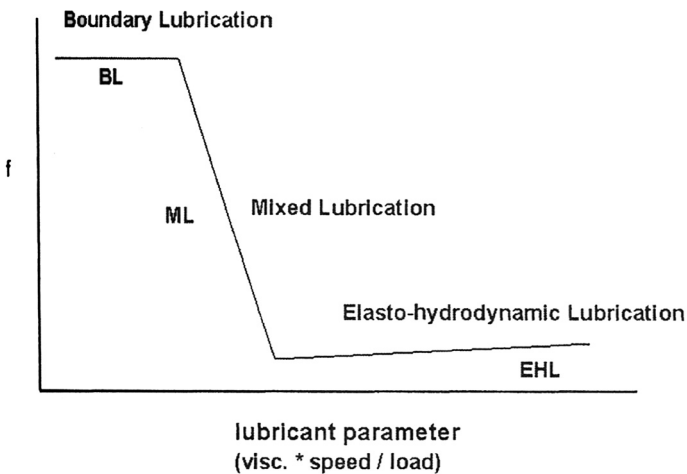


Figure 2 Stribeck curve at low contact pressure.

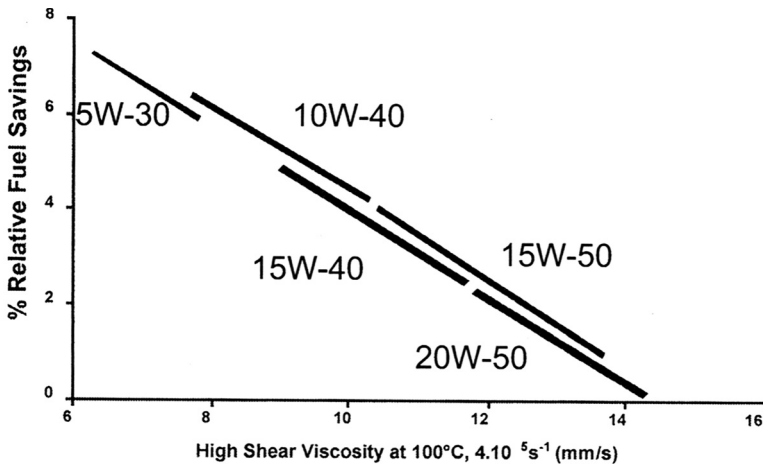


Figure 3 Relationship between SAE viscosity grades and fuel savings based on fleet car trials.

2.1 Friction Reduction Through the Lubricant

Engine friction originates from several components, which operate at different conditions of load, speed, and temperature. Hence, these components may experience various combinations of elasto-hydrodynamic, mixed, and boundary lubrication during engine operation. For each of these regimes, a number of factors govern engine friction.

Basically, two options to reduce friction and to improve fuel efficiency come forward [7,8].

1. Use of low-viscosity engine oils (SAE 0W/5W-20/30) when fluid lubrication (elasto-hydrodynamic regime) is the governing factor [9–11]. Fluid lubrication is especially prevalent in the bearings. The gradual reduction of engine oil viscosity over the years has already brought significant fuel savings (see Figure 3).

In the above case, base oil selection is crucial. In terms of fractional characteristics, one must emphasize low kinematic viscosity, high viscosity index, low “high-temperature, high-shear” (HTHS) viscosity, and a low-pressure/viscosity coefficient [12,13]. However, it has to be realized that other base fluid properties, such as volatility and thermal/oxidation stability, must not be ignored.

2. Addition of friction-reducing agents when boundary and/or mixed lubrication are the governing factors [14]. These are prevalent in the valve train and the piston group.

In this case, additive system design is the crucial factor. One must emphasize selecting proper friction modifiers and control of additive-additive and additive-base fluid interactions.

In order to assess possible fuel economy improvements in the engine sequences prescribed, an overview is given of the lubrication regimes existing in the various test

Table 1 Lubrication Regimes in API Sequences VI and VIA

	API Sequence VI (%)	API Sequence VIA (%)
Boundary lubrication	37	24
Mixed lubrication	15	4
Elasto-hydrodynamic lubrication	48	72

engines. For those used for current and previous ILSAC specifications, the data are given in Table 1.

In Sequence VIA, which is prescribed for ILSAC GF-2, elasto-hydrodynamic lubrication is dominating, leading to a substantial effect of engine oil viscosity on fuel economy. Effects of friction modifiers will be small due to the low presence of boundary and mixed lubrication conditions, which is due to the application of roller followers. Hence, the Sequence VIA test engine is often indicated as “as a very expensive viscometer.”

This characterization of the Sequence VIA engine will be addressed by Sequence VIB, to be used for ILSAC GF-3, for which an engine with a bucket tappet sliding valve train will be used, leading to an increase of the boundary and mixed lubrication regimes [3].

In Europe the M111 engine is used for the CEC L-54-T-96 fuel economy test, which is prescribed in the ACEA A1 and B1 engine oil specifications. Similar data as above are not available to the authors, but data given in a Shell paper [15] indicate the frictional losses occurring in this engine, which can be translated to lubrication regimes (Table 2).

Based on the relatively high amount of frictional losses in the valve train and piston assembly, the M111 engine should be sensitive to friction modifiers. This is due to the use of four valves per cylinder in order to improve combustion efficiency and so to obtain more power from a given amount of fuel.

However, compared to other engine designs, the frictional losses in the M111E valve train will be higher. Provided that the higher-power output obtained from the four-valve assembly is significantly higher than is lost by higher valve train friction, this approach is favorable with regard to fuel economy.

3 FRICTION MODIFIERS (FM) VERSUS ANTIWEAR/EXTREME-PRESSURE ADDITIVES

A point of debate is often about the difference between friction modifiers and anti-wear/extreme-pressure (AW/EP) additives, especially when it is about friction modi-

Table 2 Lubrication Regimes in the DB M111E Engine

	Frictional losses (%)	Main lubrication regime
Valve train	25	boundary lubrication
Piston assembly	40	mixed lubrication
Bearings	35	elasto-hydrodynamic lubrication

Table 3 Lubrication Modes Versus Friction Coefficient

Lubrication mode	Friction coefficient	Comparison
Nonlubricated surface	0.5–7	Dragging an irregular rock over rocky ground
Antiwear/EP films	0.12–0.18	Dragging a flat stone over a flat rock
Friction-modified films	0.06–0.08	Ice skating
Elasto-hydrodynamic lubrication	0.001–0.01	Hydroplaning

fiers active at boundary lubrication conditions. For a good understanding, this should be clarified; therefore, this section deals with the principal difference between these two additive categories [16].

AW/EP additives are types of compounds that provide good boundary lubrication. Such materials have the capacity to build strong boundary lubrication layers under severe load conditions. Hence, AW/EP additives protect closely approaching metal surfaces from asperities damaging the opposite surface. On the other hand, most antiwear additives have little friction-modifying properties.

The crucial differences between AW/EP and FM films are their mechanical properties. AW/EP films are semiplastic deposits that are difficult to shear off. So, under shearing conditions their coefficient of friction is generally moderate to high. Conversely, friction-modified lubricant films are built up of orderly and closely packed arrays of multimolecular layers, loosely adhering to each other and with the polar head anchored on the metal surface. The outer layers of the film can be easily sheared off, allowing for a low coefficient of friction.

The difference between the two types of films and other lubrication modes is best illustrated by the data presented in Table 3.

4 CHEMISTRY OF ORGANIC FRICTION MODIFIERS

Organic friction modifiers are generally long, slim molecules with a straight hydrocarbon chain consisting of at least 10 carbon atoms and a polar group at one end. The polar group is one of the governing factors in the effectiveness of the molecule as a friction modifier. Chemically, organic friction modifiers can be found within the following categories [16]:

- Carboxylic acids or their derivatives, e.g., stearic acid, partial esters
- Amides, imides, amines, and their derivatives, e.g., oleylamide
- Phosphoric or phosphonic acid derivatives
- Organic polymers, e.g., methacrylates

Another classification can be given by mode of action and friction modifier type (Table 4).

Due to the different mode of actions, the mechanism of friction reduction varies for each category.

The next section further deals with details about their mode of action, and another section deals with the current chemistry used as well as specific products.

Table 4 Friction Modifier Type and Mode of Action

Mode of action/type of FM	Products
Formation of reacted layers	Saturated fatty acids, phosphoric- and thiophosphoric acids, sulphur-containing fatty acids
Formation of absorbed layers	Long-chain carboxylic acids, esters, ethers, amines, amides, imides
Formation of polymers	Partial complex esters, methacrylates, unsaturated fatty acids, sulphurized olefins
Mechanical types	Organic polymers

4.1 Friction Modifier Mechanisms

4.1.1 Formation of Reacted Layers

Similar to antiwear additives, protective layers are formed by chemical reaction of the additive with the metal surface. However, the principal difference is that the reaction has to occur under the relatively mild conditions (temperature, load) of the mixed lubrication regime. These conditions require a fairly high level of chemical activity as reflected by the phosphorus and sulphur chemistry applied.

An exception to this is stearic acid. Theoretically, the friction-reducing effect of stearic acid should decrease with increasing temperature due to desorption of the molecule from the metal surface. However, stearic acid experimentally shows a remarkable drop of friction with increasing temperature, which can only be explained by the formation of chemically reacted protective layers.

4.1.2 Formation of Absorbed Layers

The formation of absorbed layers occurs due to the polar nature of the molecules. Friction modifiers dissolved in oil are attracted to metal surfaces by strong absorption forces, which can be as high as 13 kcal/mole. The polar head is anchored to the metal surface and the hydrocarbon tail is left solubilized in the oil, perpendicular to the metal surface (see [Figure 4](#)). Next the following steps occur:

Other friction modifier molecules have their polar heads attracted to each other by hydrogen bonding and Debye orientation forces, resulting in dimer clusters. Forces are about 15 kcal/mole.

van der Waals forces cause the molecules to align themselves such that they form multimolecular clusters that are parallel to each other.

The orienting field of the absorbed layer induces further clusters to position themselves with their methyl groups stacking onto the methyl groups of the tails of the absorbed monolayer [17,18].

As a result, all molecules line up straight, perpendicular to the metal surface, leading to a multilayer matrix of friction modifier molecules (see [Figure 5](#)).

The FM layers are difficult to compress but very easy to shear at the hydrocarbon tail interfaces, explaining the friction-reducing properties of friction modifiers. Due to the strong orienting forces mentioned above, sheared-off layers are quite easily rebuilt to their original state.

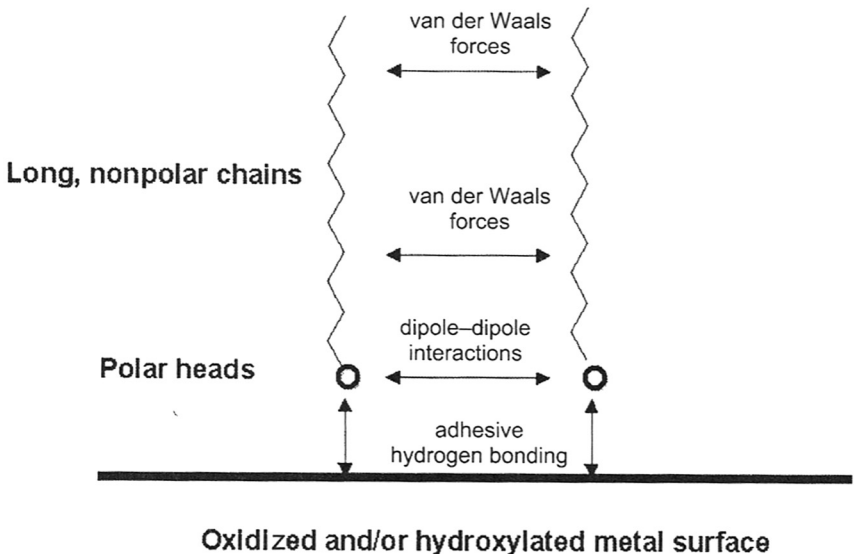


Figure 4 Organic friction modifiers—formation of adsorbed layers.

The thickness and effectiveness of the absorbed friction modifier films depend on several parameters, four of which we explain here.

Polar Group

Polarity itself is not necessarily sufficient for adsorption; the polar group must also have hydrogen-bonding capability. Molecules with highly polar functional groups

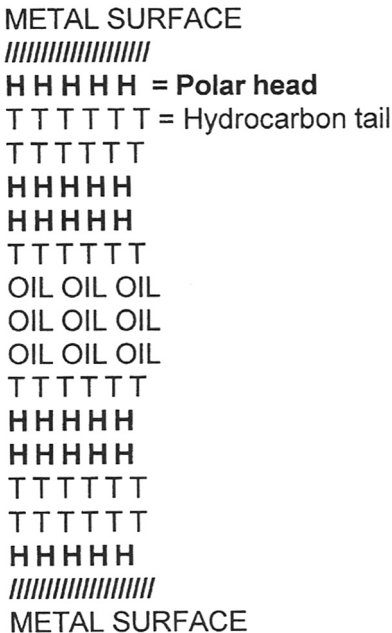


Figure 5 Multilayer matrix of friction modifier molecules.

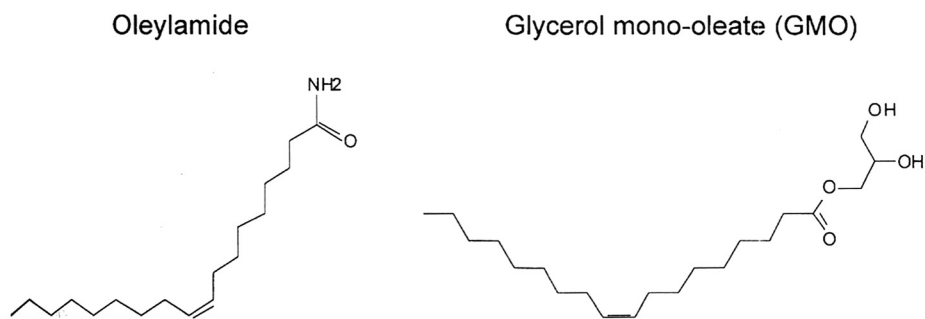


Figure 6 Organic friction modifiers—structural drawings.

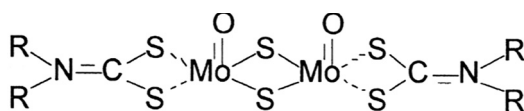


Figure 7 Molybdenum dithiocarbamate—structural drawing.

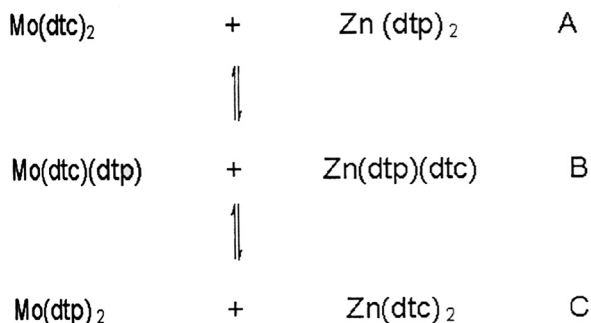


Figure 8 Molybdenum dithiocarbamate—exchange of functional groups.

that are not capable of forming hydrogen bonds, such as nitroparaffins, do not adsorb. Hence, these do not function as friction-reducing additives. However, polarity plays a major role among the various lateral surface interactions through strong electrostatic dipole–dipole interactions. These may be either repulsive or attractive, depending on the orientation of the adsorbed dipoles with respect to the surface [19].

Chain Length

Longer chains increase thickness of the adsorbed film while interactions between the hydrocarbon chains increase as well [18].

Molecule Configuration

Slim molecules allow for closer packing as well as increased interaction between adjacent chains, leading to stronger films. Therefore, straight chains may be preferred.

Temperature

Temperature influences friction modifier film thickness and tenacity. Adsorption of friction-reducing compounds to the metal surface does occur at relatively low temperatures. Antiwear additives from protective layers by chemical reactions for which higher temperatures are needed.

If the temperature is too high, enough energy might be provided to desorb the friction-reducing molecules from the metal surface.

4.1.3 Formation of In Situ Polymers

The formation of low-friction-type polymer films can be considered a special case. Instead of the usual solid films, fluid films are formed under influence of contact temperature (flash temperature) and load. Another difference is that the polymers are developed at the contact interface between metal asperities without reacting with the metal surface.

The requirements of such polymers are

Relatively low reactivity: polymerization must be generated by frictional energy.

The polymers formed have to be mechanically and thermally stable and should not be soluble in the lubricant.

The polymers must develop a strong bond to the metal surface either by absorption or by chemical bonding.

The formation and regeneration of films must be fast to prevent competitive adsorption by other additives.

Examples of polymer-forming friction modifiers are

Partial complex esters, e.g., a sebacic acid/ethylene glycol partial ester

Methacrylates

Oleic acid (olein), which may be explained through thermal polymerization (formation of dimers and higher oligomers)

5 CHEMISTRY OF OTHER FRICTION MODIFIERS

Within this group, the following categories can be distinguished by chemical type:

Metallo-organic compounds

Oil-insoluble materials

Classification by type appears in [Table 5](#).

5.1 Metallo-organic Compounds

Examples of friction-reducing metallo-organic compounds are molybdenum-dithiophosphate, -dithiocarbamate, and -dithiolate as well as copper-oleate, -salicylate, and -dialkyldithiophosphate.

Table 5 Classification of Other Friction Modifiers

Type of friction modifiers	Products
Metallo-organic compounds	Molybdenum and copper compounds
Mechanical types	Molybdenum disulphide, graphite, teflon (PTFE)

The mechanisms of operation of this class of products are not fully understood, but the following hypotheses are presented:

Diffusion of molybdenum into the asperities

Formation of polymer-type films

In situ formation of molybdenum disulphide (most accepted hypothesis)

Selective transfer of metal (copper) leading to the formation of thin, easy-to-shear metal films

5.2 Mechanical Types

In this group the classical types such as graphite and molybdenum disulphide can be found as well as some more recent friction modifiers such as teflon (polytetrafluoroethylene, PTFE), polyamides, fluoridized graphite, and borates. The friction-reducing mechanisms can be explained by

The stratified structure and formation of easy-to-shear layers

The formation of elastic or plastic layers on the metal surface

6 FACTORS INFLUENCING FRICTION-REDUCTION PROPERTIES

This section lists the main factors that impact friction-reducing properties.

Competing Additives

Other polar additives with affinity to metal surfaces such as AW/EP and anticorrosion additives as well as detergents and dispersants may compete with friction modifiers. This emphasizes that lubricant formulations have to be balanced carefully to achieve optimal performance.

Contaminants

Short-chain acids, which are formed by oxidative degradation of the lubricants, may compete at the metal surface, resulting in a loss of friction-modifying properties.

Metallurgy

The type of steel alloy used will affect the adsorption of friction modifiers.

Concentration

Increase of friction modifier concentration results in an increase of friction reduction up to a point above which improvements are marginal. Generally, the friction-reducing effect is most (cost-) effective at concentrations of about 0.25% up to 1% for organic friction modifiers and 0.05–0.07% for molybdenum for molybdenum dithiocarbamates.

7 FRICTION MODIFIERS—CURRENT PRACTICE

The most frequently used organic friction modifiers include

1. Long-chain fatty amides, specifically oleylamide (Figure 6). This is a reaction product of olein (main component oleic acid, a straight-chain unsaturated C18 carboxylic acid) and ammonia (NH_3).
2. Partial esters, specifically glycerol mono-oleate (GMO) (Figure 6). GMO is a reaction product of glycerin (a natural alcohol with three hydroxyl groups) and olein (as above). Investigations have shown that the alpha version (terminal hydroxyl groups esterified) is the active component rather than the beta one (middle hydroxyl group esterified). Special production techniques are required to manufacture high-alpha-containing products.

The mode of action of both product groups is based on the formation of adsorbed layers that can easily be sheared off, leading to reduced friction. It is expected that further research will result in new and improved types in order to cope with more severe requirements with regard to friction retention over time.

Within the group of metallo-organic compounds, molybdenum dithiocarbamate $[\text{Mo}(\text{dth})_2]$ seems almost exclusively to be used to obtain friction reduction (Figure 7). Research [7,20] has shown that the friction-reducing activity of $\text{Mo}(\text{dth})_2$ is based on the exchange of functional groups with zinc dialkyldithiophosphates $[\text{Zn}(\text{dtp})_2]$ (Figure 8).

It was found that oxidation significantly affects these exchange reactions and that the most effective friction reduction is achieved at the later stages of oxidation when the concentrations of the single-exchange product $[\text{Mo}(\text{dth})(\text{dtp})]$ and the double-exchange product $[\text{Mo}(\text{dtp})_2]$ are high. When both products are nearly consumed by oxidation, friction reduction ceases.

8 FRICTION MODIFIER PERFORMANCE

Literature suggests that friction modifiers act both in the boundary lubrication regime and in the mixed lubrication regime [7,16,21]. Their mode of action should depend on friction modifier chemistry and prevailing engine conditions. It is further suggested that organic friction modifiers are most active in the mixed regime, whereas metallic types are predominantly active in the boundary regime. Recent investigations by the authors, carried out with a pin-on-ring tribometer, showed that it is likely that organic friction modifiers act predominantly in the boundary regime as well.

Tests were carried out with CEC reference oil RL 179/2, which is applied in the CEC L-54-T-96 Fuel Economy Test. RL 179/2 is a formulated 5W/30 engine oil that does not contain any friction modifier and that has a proven fuel economy benefit in CEC round-robin tests.

Frictional behavior was investigated by establishing stabilized Stribeck curves. By determining these, both boundary and mixed friction can be investigated. Stabilized Stribeck curves are obtained by measuring the coefficient of friction over a speed range from about 0.0025 to 2 m/sec at appropriate steps. A number of runs are carried out until two consecutive runs give a good match. Usually, after four runs the curve has stabilized, meaning that process roughness has stabilized to a large extent.

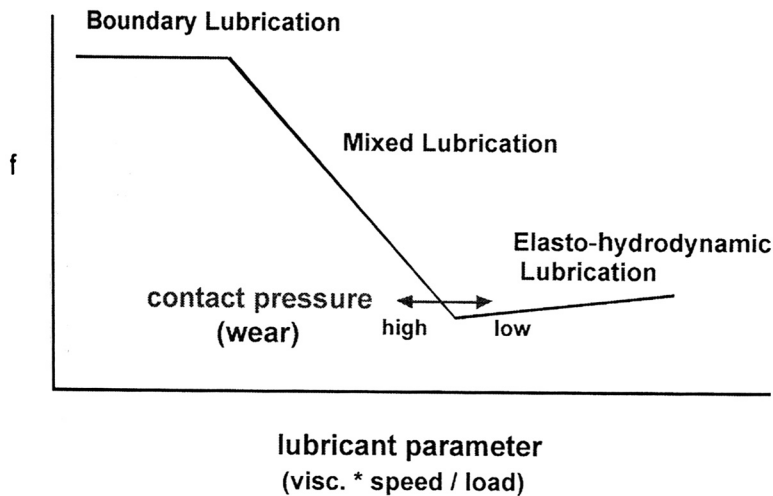


Figure 9 Influence of wear/contact pressure on ML/EHL transition.

Performance criteria in considering the results are frictional level in the boundary and mixed lubrication regimes in combination with specimen wear. The reason for looking at wear is that this parameter corresponds with contact pressure, which in turn has influence on the ML/EHL transition.

The relationship between wear and contact pressure is given by the expression

$$F_n/A = p \quad (7.3)$$

where

F_n = the normal force (load).

A = the wear scar.

p = the contact pressure.

Consequently, a high-wear scar leads to a lower contact pressure, while a lower contact pressure does shift the ML/EHL transition in the Stribeck curve to the left (see Figure 9).

8.1 Stribeck Curve Determinations

Stabilized Stribeck curves have been determined with a pin-on-ring tribometer at which the ring was a 100Cr6 stainless steel ring with a 730-mm diameter. These rings are high-quality materials used in standard bearings and therefore easily available. The pin used was a cylinder from the same material with an 8-mm diameter, also used in bearings. To get proper line contact, the cylinders have been provided with "flexible" ends to allow full alignment with the ring.

Ring roughness, R_a , was about 0.15 micron, while the cylinder was very smooth. Hence, the roughness of the ring was determining the shape of the Stribeck curve, specifically the BL/ML transition. The load (normal force $F_n = 100$ Newton) was chosen such that heat development in the contact zone was negligible so that the viscosity was constant. Hence, it was possible to determine the Stribeck curve only as a function of speed. The temperature chosen was 40°C.

The following graph (Figure 10) shows comparative data for RL 179/2 as well as this oil with addition of 0.5% GMO (glycerol mono-oleate) and addition of 0.5% of organic friction modifiers A and B. (A and B are products with both free and esterified hydroxyl groups.)

All the friction modifiers studied here show a significant reduction of the friction coefficient in the boundary regime. Organic friction modifiers A and B show a reduction in the mixed regime as well. On first sight this looks favorable.

The next graph (Figure 11) shows the wear, taken at similar sliding distances.

The wear of the oil containing A and B is twice as high as those of the reference oil and that oil with addition of 0.5% GMO. Consequently, the contact pressure p is twice as low as those of the others and is what makes the ML/EHL transition shift to the left.

So it seems that organic friction modifiers are predominantly active in the boundary regime and that the shifts observed in the mixed regime are likely to be caused by other phenomena that must not be ignored.

8.2 Friction as a Function of Temperature

Another aspect of friction modifier performance is friction as a function of temperature. Temperature plays an important role with regard to adsorption/desorption phenomena as for the formation of adsorbed layers as well as regarding those of reacted layers.

The graph in Figure 12 shows the frictional behavior of some organic friction modifiers as a function of temperature, using the pin-on-ring tribometer as before with the same specimens and configuration. Again, CEC reference oil RL 179/2 was used and the speed chosen (0.03 m/sec) assured operation well within the boundary regime.

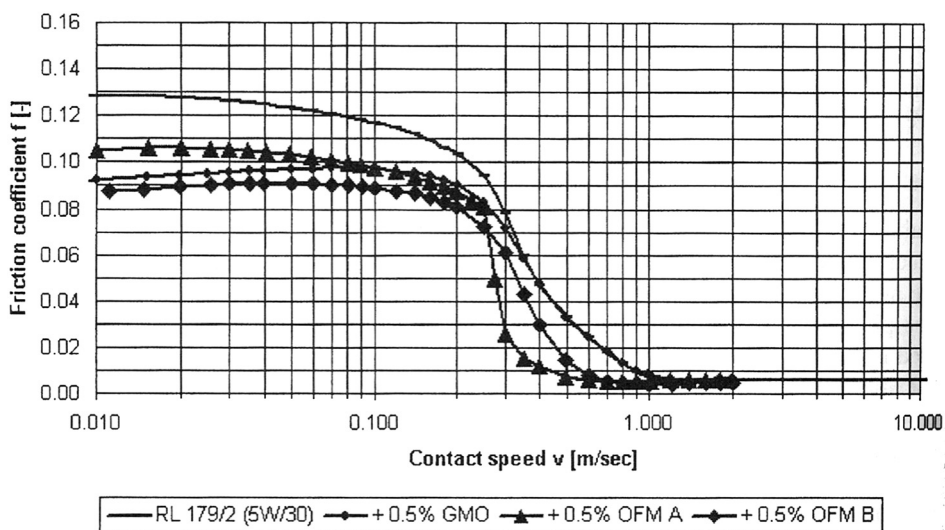


Figure 10 Stribeck curves of CEC RL 179/2 plus organic friction modifiers.

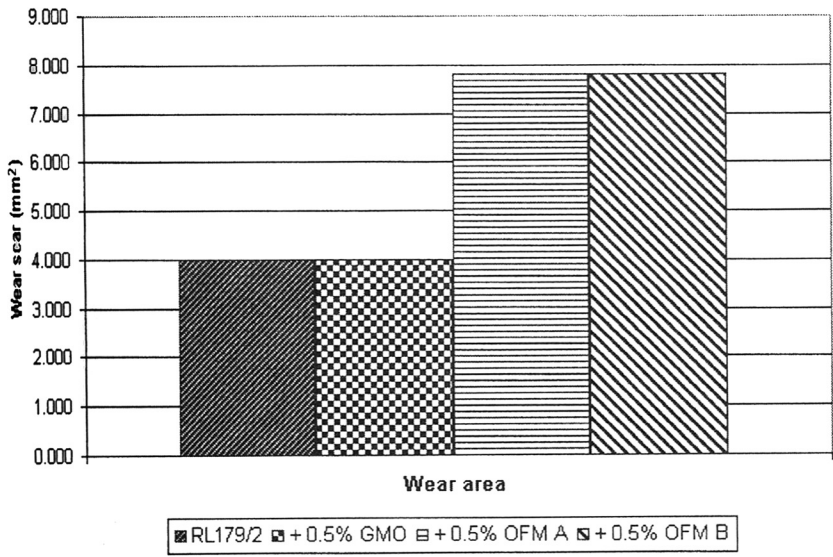


Figure 11 Wear scars of CEC RL 179/2 plus organic friction modifiers.

All the organic friction modifiers studied show a significant friction reduction over the temperature range tested. Glycerol mono-oleate and oleylamide perform best, and the optimum adsorption seems to be obtained at about 70°C. At higher temperatures, desorption may start to occur as well as some kind of competition with

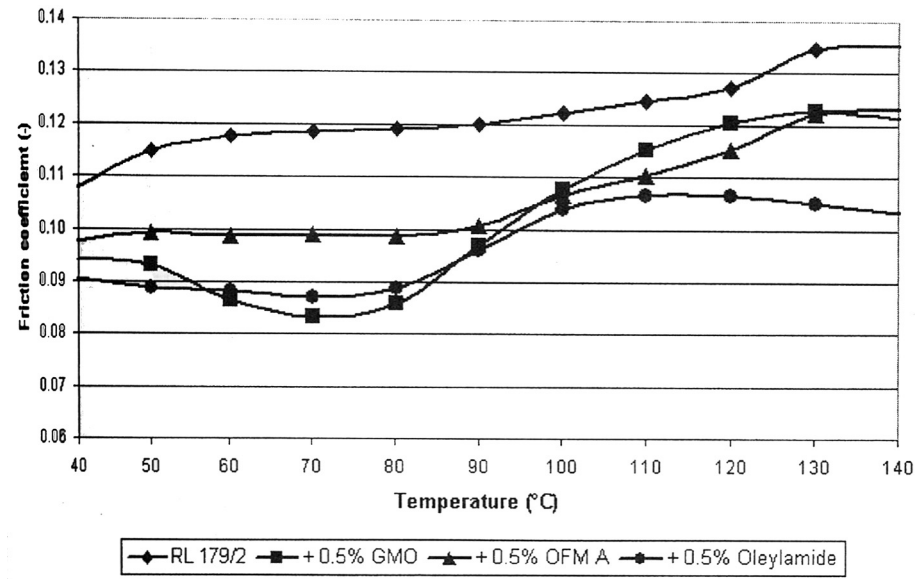


Figure 12 Friction coefficient versus temperature—CEC RL 179/2 plus organic friction modifiers.

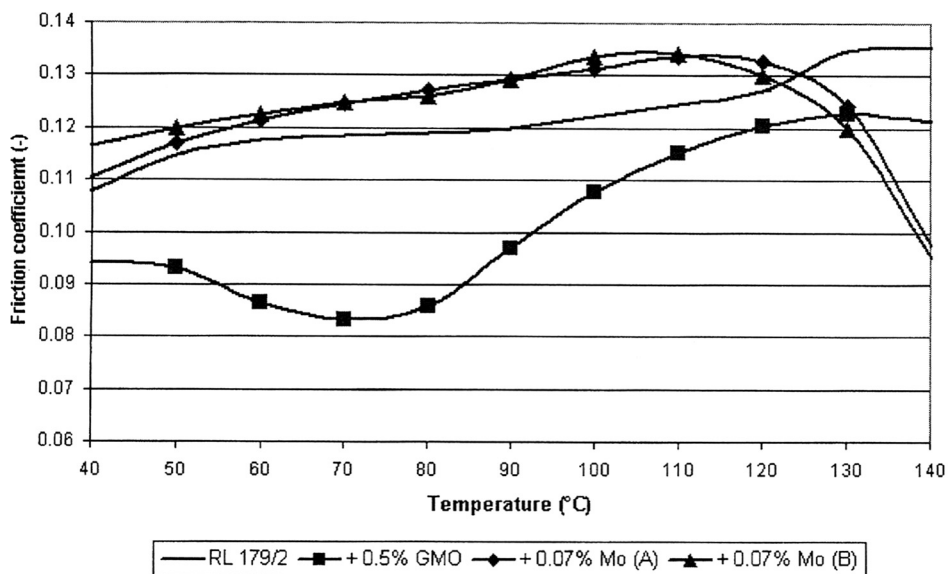


Figure 13 Friction coefficient versus temperature—CEC RL 179/2 plus molybdenum dithiocarbamates.

other surface-active additives, leading to a higher coefficient of friction. Oleylamide, however, continues to show high friction-reducing properties at elevated temperatures.

Figure 13 shows a comparison between organic friction modifier Glycerol mono-oleate and metallic-type friction modifier molybdenum dithiocarbamate. Two sources of the latter were used at a concentration equivalent to 0.07% molybdenum.

Glycerol mono-oleate and the molybdenum dithiocarbamates show a marked performance difference. Whereas GMO is active over a wide temperature range, the molybdenum dithiocarbamates start to reduce friction at temperatures of 120°C and above only. This has to be considered as an induction period that can be explained by the necessary exchange of ligands between molybdenum dithiocarbamate and zinc dialkyldithiophosphate (see [Section 7](#), above). Once molybdenum dithiocarbamate has “lighted off,” a fast drop of friction is noticed. At the end of the test cycle at 140°C, the system has not stabilized and the friction coefficient might decrease further.

The difference in friction-modifying characteristics between organic friction modifiers and molybdenum dithiocarbamate suggests that it might be beneficial to use a combination of these materials.

9 CONSEQUENCES OF NEW ENGINE OIL SPECIFICATIONS AND OUTLOOK

While initial fuel economy requirements were focused on the fresh oil only, new engine oil specifications will address fuel economy longevity as well. A good example is Sequence VIB, which has been developed for the ILSAC GF-3 specification.

Sequence VIB includes aging stages of 16 and 80 hr in order to determine fuel economy as well as fuel economy longevity. These aging stages are equivalent to 4000–6000 miles of mileage accumulation required prior to the EPA Metro/High-Highway Fuel economy test. That test is used in determining corporate average fuel economy (CAFE).

To obtain engine oil formulations that are optimized with regard to fuel economy longevity, high requirements are demanded for base oil selection and additive system design [3,7,22]. These requirements are

- To minimize the increase of viscosity
- Thereby maintaining a low (E)HD friction coefficient
- To maintain low boundary/mixed friction

A minimum increase of viscosity can be obtained by base fluid selection (in terms of volatility, oxidation stability, and antioxidant susceptibility) and selection of antioxidants and their treat level. The market is already anticipating these requirements by increasing the production capacity of Groups II (HVI) and III (VHVI) base fluids and by increased interest in Groups IV (PAOs) and V (a.o. esters) base fluids.

To achieve low friction under boundary and mixed lubrication conditions, the use of effective friction-reducing additives is needed. To maintain low boundary and mixed friction over time, it is necessary to prevent consumption of these additives by processes such as oxidation and thermal breakdown. Therefore, selecting suitable antioxidant systems for molybdenum compounds and organic friction modifiers and developing organic friction modifiers with highest thermal/oxidative stability will be key for high fuel economy longevity and a successful application in engine oil formulations.

Further studies on the mechanisms of friction modifier action, e.g., through molecular modeling techniques, could also speed up the development of optimized additives and/or additive systems. Apart from frictional properties, other important tribological parameters such as wear rate and surface-metal geometry should be investigated as well. In most papers studied, this seems to be ignored, although all three parameters should be considered in relation to each other.

10 BENCH TESTS TO INVESTIGATE FRICTION-REDUCING COMPOUNDS

Several bench tests can be thought of to investigate the frictional properties of base fluids and formulated products. In recent literature [8,23,24] the following test equipment has been used:

1. The high-frequency reciprocating rig (HFRR) to measure boundary friction. Although originally developed to measure diesel fuel lubricity, the equipment can be successfully applied to measure lubricant properties as well.

Frequency	10–200 Hertz
Stroke length	20–2000 micron
Load	0–1000 g
Temperature	ambient–200°C

Specimens are a 6-mm-diameter ball as upper specimen and a 3-mm-thick smooth disk with a 10-mm diameter as the lower specimen. HFRR specifications are as follows:

Test conditions the authors applied to screen friction modifiers include a 40-Hertz frequency, a stroke of 1000 micron, and a 400-g load.

2. A mini traction machine (MTM) to measure mixed and (E)HD friction, e.g., by determination of Stribeck curves. The MTM rig is capable of measuring at either constant or varying slide/roll ratios if required.

Standard specimens are a 19.05-mm-diameter ball as upper specimen and a

Speed range	up to 5 m/sec
Slide/roll ratio	0–200% (full rolling to full sliding)
Load	0–75 Newton
Temperature	ambient–150°C

50-mm-diameter disk as lower specimen. Both are manufactured from AISI 52100 bearing steel. The standard disk is smooth, which allows measurement of mixed-film and full-film friction. Alternatively, rough disks are available for measurements in the boundary lubrication regime. MTM specifications are as follows:

Test conditions the authors applied to test friction modifiers comprise a speed range of 0.001 to 4 m/sec, a 30-Newton load, and a 200% slide/roll ratio.

3. An optical rig provided with a disc coated with a spacer layer to measure EHD film thickness. Such a rig enables film-thickness measurements down to less than 5 nanometers with a precision between 1–2 nanometers.

Some other literature refers to the LVFA (low-velocity friction apparatus). Alternative reciprocating rigs may be suitable as well.

REFERENCES

1. MA Wilk, WD Abraham, BR Dohner. An investigation into the effect of zinc dithiophosphate on ASTM sequence VIA fuel economy. SAE Paper 961,914, 1996.
2. M Houben. Friction analysis of modern gasoline engines and new test methods to determine lubricant effects, 10th Intl Colloquium, Esslingen, 1996.
3. S Korcek. Fuel efficiency of engine oils—current issues. 53rd Annual STLE Meeting, Detroit, 1998.
4. A LaFountain, GJ Johnston, HA Spikes. Elastohydrodynamic friction behavior of poly-alphaolefin blends, Tribology Series 34:465–475, 1998.
5. HA Spikes. Boundary lubrication and boundary films. Tribology Series 25:331–346, 1993.
6. HA Spikes. Mixed lubrication—an overview. Lubrication Science 9(3):221–253, 1997.
7. S Korcek et al. Retention of fuel efficiency of engine oils, 11th Intl Colloquium, Esslingen, 1998.

8. J Sorab, S. Korcek, C Bovington. Friction Reduction in lubricated components through engine oil formulation. SAE Paper 982,640, 1998.
9. MC Goodwin, ML Haviland. Fuel economy improvements in EPA and road tests with engine oil and rear axle lubricant viscosity reduction. SAE Paper 780,596, 1978.
10. WE Waddey et al. Improved fuel economy via engine oils. SAE Paper 780,599, 1978.
11. JE Clevenger, DC Carlson, WM Keiser. The effects of engine oil viscosity and composition on fuel efficiency. SAE Paper 841,389, 1984.
12. GR Dobson, WC Pike. Predicting viscosity related performance of engine oils. *Erd-I und Kohle-Erdgas* 36(5):218–224, 1982.
13. J Battersby, JE Hillier. The prediction of lubricant-related fuel economy characteristics of gasoline engines by laboratory bench tests. *Proc Intl Colloquium, Technische Akademie Esslingen*, 1986.
14. DW Griffiths, DJ Smith. The importance of friction modifiers in the formulation of fuel efficient engine oils. SAE Paper 852, 112, 1985.
15. RI Taylor. Engine friction lubricant sensitivities: A comparison of modern diesel and gasoline engines. 11th Intl Colloquium, Esslingen, 1998.
16. J Crawford, A Psaila. In RM Mortier and ST Orszulik, eds. *Chemistry and Technology of Lubricants, Miscellaneous Additives*. London, 1992, pp 160–165.
17. CM Allen, E Drauglis. Boundary lubrication: Monolayer or multilayer, *Wear* 14:363–384, 1969.
18. AS Akhmatov, *Molecular physics of boundary lubrication*. Gos. Izd. Frz.-Mat. Lit., Moscow 297, 1969.
19. M Beltzer, S Jahanmir. Effect of additive molecular structure on friction, *Lubrication Science* 1-1:3–26, 1998.
20. K Arai et al. Lubricant technology to enhance the durability of low friction performance of gasoline engine oils. SAE Paper 952,533, 1995.
21. D Christakudis. Friction modifiers and their testing, *Additives for Lubricants. Kontakt Stud* 433:134–162, 1994.
22. Effects of aging on fuel efficient engine oils. *Automotive Engineering* Feb. 1996.
23. AJ Moore. Fuel efficiency screening tests of automotive engine oils. SAE Paper 932,689, 1993.
24. C Bovington, HA Spikes. Prediction of the influence of lubricant formulations on fuel economy from laboratory bench tests. *Proc Intl Tribology Conf, Yokahama*, 1995.

Ashless Antiwear and Extreme-Pressure Additives

LIEHPAO OSCAR FARNG

ExxonMobil Research and Engineering Company, Annandale, New Jersey, U.S.A.

1 INTRODUCTION

To optimize the balance between low wear and low friction, machine designers specify a lubricant with a viscosity sufficient to generate hydrodynamic or elastohydrodynamic oil films that separate the machine's interacting surfaces, but not too high to induce excessive viscous drag losses. In practice, the variety of contact types in a machine, the incidence of operating conditions beyond the design range, and the pressure to improve efficiency by reducing oil viscosity all conspire to reduce oil-film thickness below the optimum. The high spots, or asperities, on the interacting surfaces then start to interact with each other, initially through micro-EHL films, and at the extreme through direct surface contact, resulting in increased friction and the likelihood of surface damage. Antiwear and extreme-pressure (EP) additives are added to lubricating oils to decrease wear and prevent seizure under such conditions.

A common way to demonstrate the viscosity optimization is shown in [Figure 1](#), which is known as a Stribeck curve. The curve is a composite of a boundary friction curve that decreases as viscosity and, therefore, film thickness increases and a viscous friction curve that increases as viscosity and speed increase. Slightly to the right of the minimum in the curve represents a good operating target. Improving the surface finish of contacting surfaces can move the minimum in the curve to a lower viscosity range, saving energy but increasing the cost of components. The hardening or coating of surfaces can increase their durability under increased levels of contact with lower viscosity, but again at an increase in component cost. Aside from these

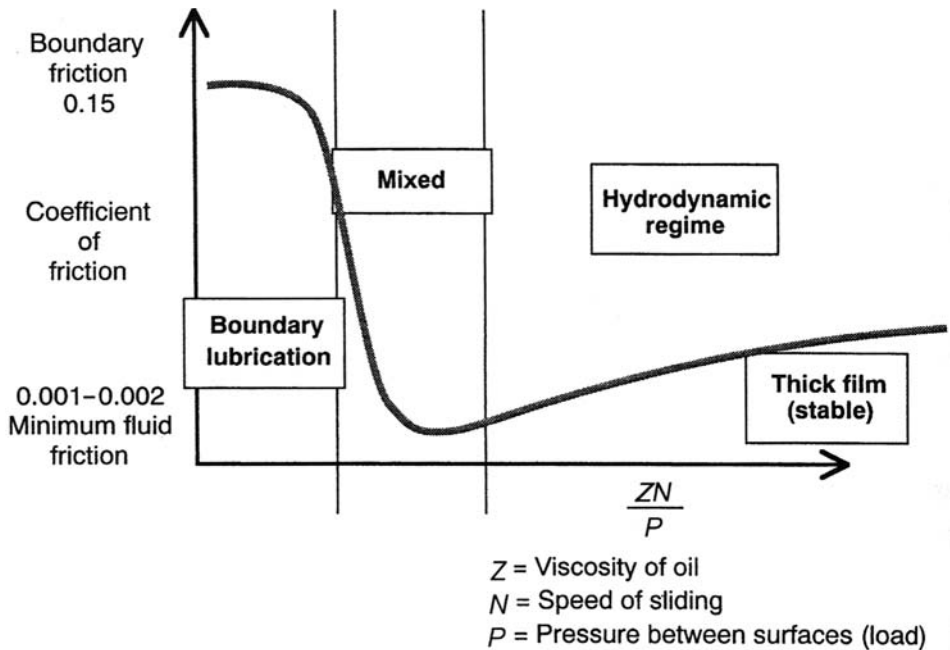


Figure 1 Regions of lubrication: Stribeck curve.

component manufacturing improvements, antiwear and EP additives will continue to be needed, but the nature of their chemistry is likely to change due to environmental constraints, component material developments, and the continuing increase in severity of machine operating conditions.

The distinction between antiwear and EP additives is not clear-cut. Some are classified as antiwear in one application and EP in another, and some have both antiwear and EP properties. To add to the confusion, EP comes in mild and strong flavors, and some EP additives are only effective in low-speed, high-load situations and others only in high-speed, high-temperature applications. Generally, antiwear additives are designed to deposit surface films under normal operating conditions and thereby reduce the rate of continuous, moderate wear whereas EP additives are expected to react rapidly with a surface under severe distress and prevent more catastrophic modes of failure such as scuffing (scoring), galling, and seizure. It has recently been suggested that EP additives be renamed “antiscuffing additives,” since there is no “pressure” distinction between them and antiwear additives, only an expectation of a performance boost under severe conditions. EP/antiscuffing additives tend to be very reactive, and some can have adverse effects on oxidative stability of oils, can be corrosive to nonferrous materials, and can reduce the fatigue life of bearing and gear surfaces. They should only be used when severe distress is a distinct possibility.

Antiwear additives function in a variety of ways. Some deposit multilayer films thick enough to supplement marginal hydrodynamic films and prevent asperity contact altogether. Some develop easily replenishable monolayer films that reduce the local shear stress between contacting asperities and are preferentially removed in place of surface material. Others bond chemically with the surface and slowly modify

surface asperity geometry by controlled surface material removal until conditions conducive to hydrodynamic film generation reappear.

EP additives are designed to prevent metal-metal adhesion or welding when the degree of surface contact is such that the natural protective oxide films are removed and other surface-active species in the oil are not reactive enough to deposit a protective film. This is most likely to occur under conditions of high-speed, high-load, and/or high-temperature operation. EP additives function by reacting with the metal surface to form a metal compound, such as iron sulfide. They act in a manner similar to that of antiwear additives, but their rate of reaction with the metal surface—and therefore the rate of EP film formation—is higher and the film itself is tougher. Some EP additives prevent scoring and seizure at high speed and under shock loads, while others prevent riding and rippling in high-torque, low-speed operations. In both cases, EP additives and surface metal are consumed, and a smoother surface is created with an improved chance of hydrodynamic action, resulting in less local distress and lower friction. In the absence of such additives, heavy wear and distress well beyond the scale of surface asperities would occur, accompanied by very high friction.

A wide variety of antiwear and EP additives is commercially available, and many other chemicals with antiwear and EP functionality have been reported in the literature and in patents. To be commercially viable, additives must be adequately soluble in lubricant formulations and reasonable in cost, must not overly reduce the lubricant's oxidative stability for increase the corrosivity of metals contacted by the lubricant [1–3]. Lead naphthenates were extensively used early in the industry's history, but environmental concerns have led to their virtual disappearance. Similarly, chlorine-containing additives are in decline. Zinc dialkyldithiophosphates (ZDDP or ZnDTP) are the best known and most widely used antiwear additives in engine oils, transmission fluids, and hydraulic oils. However, the concern for phosphorus poisoning of automotive catalysts and for zinc as an environmental contaminant has resulted in a pressure to find metal- and phosphorus-free replacements for both automotive and industrial applications. This had resulted in a move toward ashless antiwear and EP additives. This chapter covers these additives in terms of their chemistry, properties, performance characteristics, applications, marketing, sales, and outlook.

2 CHEMISTRY, PROPERTIES, AND PERFORMANCE (CLASSIFIED BY ELEMENTS)

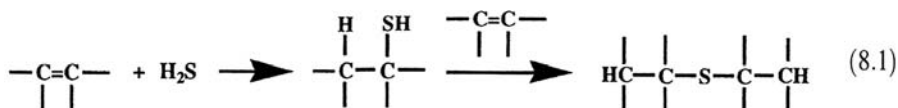
2.1 Sulfur Additives

Sulfur-containing additives are used to provide protection against high-pressure, metal-to-metal contacts in boundary lubrication. The magnitude of the extreme-pressure activity is a function of the sulfur content of the additive; high-sulfur-content additives are usually more effective extreme-pressure agents than low-sulfur-content additives. The sulfur content of the additive must be balanced against requirements for thermal stability and noncorrosiveness toward copper-containing alloys. The additive's composition and structure represent a chemical compromise between conflicting performance requirements. In general, any compound that can break down under an energy-input stress, such as heat, and allow

for a free sulfur valence to combine with iron would do well as an antiwear and EP additive. Sulfur additives are probably the earliest known, widely used EP compounds in lubricants.

Sulfurization by addition of sulfur compounds (elemental sulfur, hydrogen sulfide, and/or mercaptans) to unsaturated compounds has been known to the chemical industry for years [4–6]. The two most common classes of additives are called *sulfurized olefins* [7,8] and *sulfurized fatty acid esters* [9], because they are produced from reactions of olefins and naturally occurring or synthetic fatty acid esters with sulfur compounds.

In the absence of initiators, the addition to simple olefins is by an electrophilic mechanism, and Markovnikov's rule is followed. However, this reaction is usually very slow and often cannot be done or requires very severe conditions unless an acid catalyst is used. In the presence of free-radical initiators, H₂S and mercaptans add to double and triple bonds by a free-radical mechanism, and the orientation is anti-Markovnikov. By any mechanism, the initial product of addition of H₂S to a double bond is a mercaptan, which is capable of adding to a second molecule of olefin, so that sulfides are often produced [Eq. (1)]:

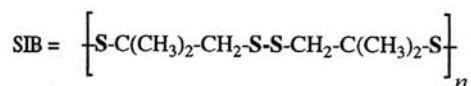
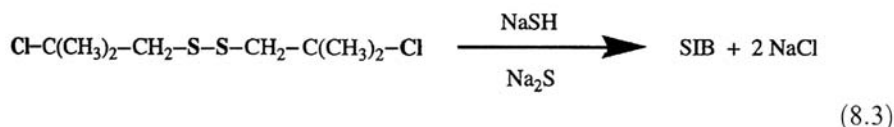
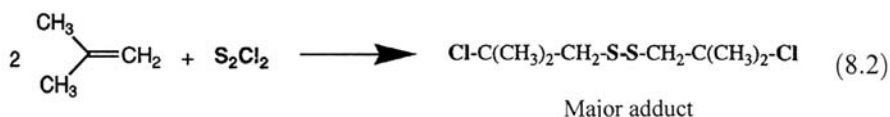


2.1.1 Sulfurized Olefins

Sulfurized olefins are prepared by treating an olefin with a sulfur source, under proper reaction conditions. The more sulfur used, the higher the sulfur content will be. Suitable olefins preferably include terminal olefins and internal olefins, mono-olefins and polyolefins. However, in order to provide adequate oil solubility, the olefin should provide a carbon chain of at least four carbon atoms. Accordingly, suitable alpha olefins are the butenes, pentenes, hexenes, and preferably higher alpha olefins such as the octenes, nonenes, and decenes. Isobutylene is a very unique olefin that not only exhibits very high reactivity toward sulfur reagents (high conversion rate), but also can produce sulfurized products having very good stability and lubricant compatibility. Therefore, sulfurized isobutylene (SIB) has been by far the most cost-effective, widely used extreme-pressure additive in lubricants.

Chemistry and Manufacture

Initially, sulfurized olefins were synthesized through a two-step chloride process, and the products were often referred to as "conventional sulfurized olefins." Sulfur monochloride and sulfur dichloride were used in the first step to produce chlorinated adducts, and then the adducts were treated with an alkali metal sulfide in the presence of free sulfur in an alcohol–water solvent, followed by further treatment with an inorganic base [Eqs. (2), (3)] [10]. The final product is a light yellow-colored fluid with oligomeric mono-sulfides and disulfides as the main compositions, as typified by

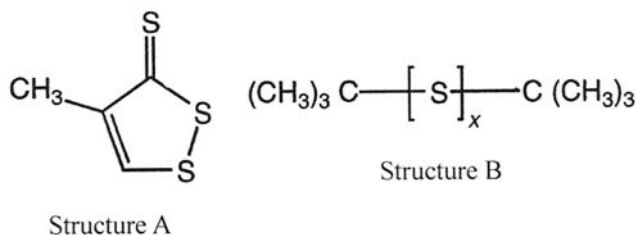


The manufacture of conventional sulfurized olefins involves sulfur monochloride, and the final product contains some residual chlorine. The process also generates aqueous waste with halogen and sulfur-containing byproducts that must be disposed of. Chlorine in lubricants and other materials is increasingly becoming an environmental concern because chlorinated dioxins can be formed when chlorine-containing materials are incinerated. Chlorinated waxes have been eliminated from many lubricants for this reason. Residual chlorine content is also becoming a major concern in many areas of the world. Germany currently has a 50-ppm maximum limit on the chlorine content of automotive gear oils. This requirement is a problem for automotive gear oil suppliers as well as for additive suppliers if their technology is based on conventional sulfurized olefins, since the residual chlorine content is a consequence of the chemistry required to manufacture conventional sulfurized olefins. By fine-tuning the manufacturing process, the chlorine content of conventional sulfurized olefins may be reduced from a typical 1500 ppm to less than 500 ppm. However, manufacturing changes to reduce the residual chlorine content will probably slow the production process, require additional capital investments, and possibly generate more aqueous waste.

In the late 1970s, the high-pressure sulfurized isobutylene (HPSIB) process was developed to replace the conventional, low-pressure, chlorine process. High-pressure sulfurized isobutylenes are usually mixtures of di-tert-butyl trisulfides, tetrasulfides, and higher-order polysulfides [11]. Some HPSIB contains oligomeric polysulfides of poorly defined composition or other materials such as 4-methyl-1,2-dithiole-3-thione (Structure A), [6,12] [Eq. (4)]. The higher-order polysulfides generally favor extreme-pressure activity at the expense of oxidative stability and copper corrosivity compared to the mono-sulfides and disulfides of conventional sulfurized olefins. In the absence of other reagents, the straight reaction of elemental sulfur and isobutylene results in a dark-colored liquid that contains a significant amount of dithiolethiones (thiocarbonates). 4-Methyl-1,2-dithiole-3-thione is a pseudo-aromatic heterocyclic compound. Due to its rigid ring structure, dithiolethione can be easily precipitated as yellowish solids that cause severe staining problems. Therefore, dithiolethione is often not a desirable side product in sulfurized isobutylene.



In the presence of various catalysts (or basic materials), such as aqueous ammonia, alkali metal sulfides, or metal dithiocarbamates, amounts of dithiolethiones and oligomeric polysulfides can be reduced and low-molecular-weight polysulfides ($X = 2$ to 6 in structure B) are the predominant products [13].



The use of hydrogen sulfide in the high-pressure sulfurized olefin process can ease the reaction complexity and also yield high-quality, low-molecular-weight polysulfides. The compositions of products prepared from this process usually have good clarity, low odor, light color, and high EP activity. Hydrogen sulfide is a very foul-smelling and toxic gas. Collapse, coma, and death from respiratory failure may come within a few seconds after one or two inhalations. Liquefied hydrogen sulfide has a high vapor pressure that requires additional, adequate protective equipment. Considerable risks are associated with its routine use on an industrial scale, but hydrogen sulfide is a low-cost, commodity chemical that can often offset the additional costs for safe use. High-pressure sulfurized olefins can also be prepared with reagents that generate hydrogen sulfide within the reactor during the course of the reaction. Direct handling of hydrogen sulfide is thus avoided, but there can be processing penalties, usually in the area of aqueous waste handling. In terms of performance, high-pressure sulfurized olefins could replace conventional sulfurized olefins in suitable applications. A decision to manufacture high-pressure sulfurized olefins by one process or another will require a careful assessment of acceptable risks versus economic requirements.

Other olefins or mixed olefins are also used in preparation of various sulfurized olefins. Among these, di-tert-nonyl and di-dodecyl trisulfides and penta-sulfides are very popular additives. Diisobutylene (2,4,4-trimethyl-1-pentene) is also used extensively to make higher-viscosity sulfurized products. In addition, sulfurized hydrocarbons, such as sulfurized terpene, sulfurized dicyclopentadiene, or sulfurized dipentene olefin, and sulfurized wax are also widely used due to low raw material costs.

Applications and Performance Characteristics

Sulfurized olefins played a key role in establishing superior ashless sulfur/phosphorus (S/P) additive systems for lubricating automotive and industrial EP gear oils in the late 1960s [14–16]. The early EP gear oil additives were clearly dominated by chlorine, zinc, and lead, which had difficulty in adequately protecting heavy-duty equipment. On the other hand, the S/P gear oil additive technology, based on ashless and chlorine-free components, possesses very good thermal-oxidative stability and rust inhibition (CRC L-33 and ASTM D 665); therefore,

this is a significant performance improvement over the metal- and chlorine-based technology.

Sulfurized olefins function mainly through thermal decomposition mechanisms. Sulfur prevents contact between interacting ferrous metal surfaces through the formation of an intermediate film of iron sulfide. By doing this, sulfur usually decreases the wear rate but accelerates the smoothing of the surfaces. This smoothing actually helps reduce the wear rate. Furthermore, a higher percent of active sulfur in a molecule increases the chances of reaction with the metal surface and favors EP (antiseizure) more than antiwear properties. Thus, sulfurized isobutylene (SIB) is mainly a strong antiscuffing additive, with outstanding scuffing protection properties (e.g., CRC L-42 performance). Table 1 shows coefficients of friction and dimensions with respect to metal surface, oil molecules, and sulfide layers. It can be seen that the friction coefficients of the sulfide layers are about half of those for metal-to-metal surfaces. The sulfide layers retard the welding of the moving metal surfaces but do not prevent wearing. Particles of iron sulfide are constantly sloughed off the metal surface. This wear can be determined by analysis of the lubricating oils (residual iron content), and subsequent sludge formation can be controlled by the use of dispersants.

Besides heavy-duty gear oil applications, sulfurized olefins have also found usefulness in other lubricant areas, such as metal-processing oils, greases, marine oils, and tractor-transmission oils.

2.1.2 Sulfurized Esters and Sulfurized Oils

The oldest widely used sulfur-based additive still found in commercial lubricants is sulfurized lard oil (SLO), a sulfurized animal triglyceride. In 1939 H. G. Smith made one of the most important discoveries in the history of lubricant additives. He found that sulfurized sperm whale oil (SSWO) was more soluble in paraffinic base oils, even at low temperatures, and had a much higher thermal stability than sulfurized lard oil. Thus, over 60 years ago, Smith recognized that the improved stability of sulfurized sperm oil resulted from its mono-ester structure, compared with the tri-ester structure of sulfurized lard oil. With long-chain mono-esters, the sulfur has little potential

Table 1 Coefficients of Friction and Dimensions for Metal Surface, Oil Molecules, and Sulfide Layers

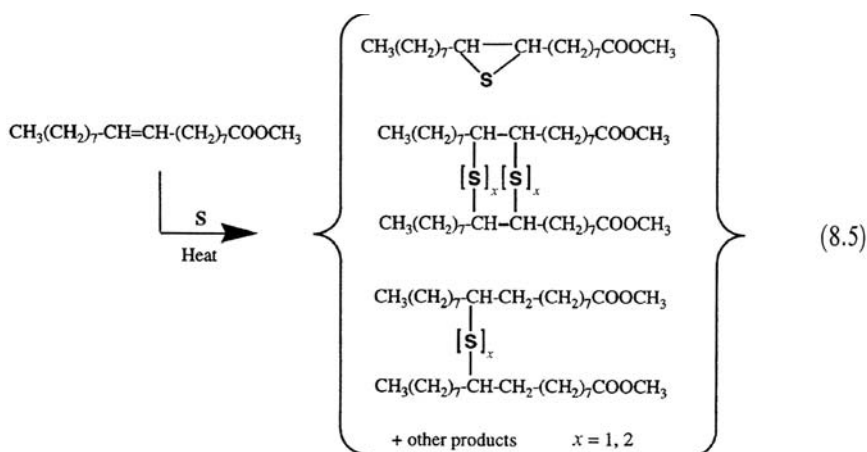
Surface	Coefficients of friction
Steel:Steel	0.78
FeS:FeS	0.39
Copper:copper	1.21
CuS:CuS	0.74
Material	Dimension(Angstrom)
Size of oil molecules	50
Size of sulfide layers	3000
Surfaces with "superfinish"	1000

to form bridges between the molecules, as it does when triglycerides are sulfurized. SSWO is an excellent boundary lubricant and is highly resistant to gumming, resin formation, or viscosity increase when subjected to high temperature and high pressure [17]. Unfortunately, from a lubricant cost-performance viewpoint, this additive is no longer available due to restrictions on the use of sperm whale oil. An available but expensive alternative is sulfurized jojoba oil, which is also a mixture of long-chain alcohol-fatty acid compounds. All these sulfurized fats or esters usually are manufactured to contain 10–15% sulfur and are often good antiwear and mild EP agents.

Chemistry and Manufacture

Sperm oil is a waxy mixture of esters of fatty alcohols and fatty acids with a small amount of triglycerides. After the separation of the solid waxes by filtration or centrifuge, a liquid wax remains, consisting mainly of an ester of oleic alcohol and oleic acid. Such a structure could not be better for sulfurizing purposes.

Similar to sulfurized olefins, sulfurized esters can be made by either direct sulfurization with elemental sulfur or sulfurization with hydrogen sulfide under superatmospheric pressures. Today they are mainly made from vegetable oils having one or more double bonds. Sulfurized esters are made from unsaturated fatty acids, like oleic acid, and esterified with an alcohol such as methanol. Frequently the sulfurization of fats is made in the presence of an olefin, preferably of long chain, and the resulting commercial product is a mixture of the two types. Equation (5) shows a typical example of sulfurization of methyl oleate with elemental sulfur. When sulfurized with hydrogen sulfide, products usually possess lighter color and lower odor.



Properties, Performance Characteristics, and Applications

The load-carrying property of sulfurized oils is directly linked to the amount of active sulfur in the additive. Percent active sulfur (which is believed to provide EP activity) and total sulfur can be determined by proper analytical methods, and the

difference is the percent inactive sulfur. The more active sulfur present, the higher the load-carrying property. However, there is also a direct correlation between active sulfur and copper corrosivity—the more active sulfur, the poorer the copper corrosion protection. The more active sulfur can also lead to cleanliness and stability challenges. Therefore, the ultimate product properties for a specific lubricant product will dictate which sulfurized products to use.

Although the sulfur content may not be as high as in many sulfurized olefins, sulfurized esters are attractive for their exceptionally good frictional properties in many applications. This is because combining sulfur with fat in a lubricant additive provides a synergistic effect. In this instance, the fat provides reduced friction, and sulfur provides wear and EP protection. Of all the elements, sulfur probably gives the best synergistic results in combination with other components and organic compounds. As to EP characteristics, sulfurized esters have a surface activity conferred by a small amount of their normal free fatty acids. These are polar species that tend to be absorbed in layers of molecular dimensions at the metal interface. The interposition of such films is effective in preventing metal seizure under conditions of extreme pressure or under conditions tending to displace the lubricating film between the bearing surfaces. Here, film strength and extreme-pressure phenomena are often used synonymously. Film strength implies that metal-to-metal contact and welding are prevented as a result of the film formation (or replenishment) by the chemical reaction of the metal and an EP additive. Also, fatty oils and sulfurized fatty oils because of their affinity for metal surfaces are less easily displaced from metal surfaces by water than are mineral oils.

The ferrophilic ester groups improve the EP properties. Depending on the molecular structure and its polarity, the surface activities vary. Since the surface activity or polarity of the substances used for sulfurization plays an equally decisive role in lubricating action, it should be taken into serious consideration when one formulates a product for a specific application. Comparing sulfurized triglycerides (e.g., SLO) with sulfurized monoesters (e.g., SSWO), we see that the EP properties of the triglycerides are better. Two factors may be responsible for this phenomenon: (1) as the triester structure is more ferrophilic, hydrogen bridging may occur; (2) as triglycerides decompose at high temperatures to form acrolein moieties during the lubrication process, the polymerized acrolein film can add strength to the sulfide film and improve the EP characteristics. However, this EP activity of triglycerides has limited value due to their poor stability and oil solubility. Stability tests at elevated temperatures show faster and heavier sludging for SLO than for SSWO. Therefore, a proper balance of all properties is an essential part of product formulations.

Sulfurized fats or esters are used extensively in lubricants such as metal-working fluids, tractor-transmission fluids, and greases.

2.1.3 Other Sulfur Additives

Elemental sulfur provides good extreme-pressure properties; however, it leads to corrosion. It dissolves in mineral oils up to certain levels depending on the type of base oils. Low-polarity paraffinic/naphthenic-type Groups II and III base oils usually have very limited solubility of elemental sulfur. Sulfurized aromatics such as dibenzyl disulfide, butylphenol disulfide, diphenyl disulfide, or

tetramethyldibenzyl disulfide generally containing less active sulfur improve only moderately the extreme-pressure characteristics of lubricants; they are therefore used predominantly in combinations with other sulfur or phosphorus-containing EP additives [18,19]. Other sulfur carriers such as sulfurized nonylphenol, dialkyl thiodipropionates ($S[CH_2CH_2C(=O)OR]_2$) derivatives of thioglycolic acid esters ($HS-CH_2C(=O)OR$), and trithians are also available. However, materials with low sulfur content are usually less active as antiwear/EP additives but more effective as antioxidants.

2.2 Phosphorus Additives

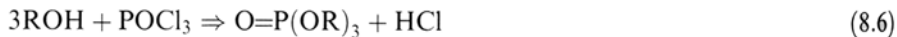
Phosphorus-containing additives are used to provide protection against moderate- to high-pressure, metal-to-metal contacts in boundary lubrication, and elasto-hydrodynamic lubrication (EHL). Unlike sulfur additives, where their extreme-pressure activity must be balanced against performance requirements for thermal stability and mild corrosivity toward copper-containing alloys, phosphorus additives usually possess very good corrosivity control. Due to totally different mechanisms involved in surface film formation rates and film strengths, phosphorus additives cannot replace sulfur additives in many applications, and vice versa. Typically, phosphorus additives are extremely effective in applications with slow sliding speeds and high surface roughness.

2.2.1 Phosphate Esters

Phosphate esters have been produced commercially since the 1920s and have gained importance as lubricant additives, plasticizers, and synthetic base fluids for compressor and hydraulic oils. They are esters of alcohols and phenols with a general formula $O=P(OR)_3$, where R represents alkyl, aryl, alkylaryl, or very often, a mixture of alkyl and aryl components. The physical and chemical properties of phosphate esters can be varied considerably depending on the choice of substituents, and these can be selected to give optimum performance for a given application. Phosphate esters are particularly used in applications that benefit from their high-temperature stability and excellent fire-resistance properties in addition to their adequate antiwear properties [20].

Chemistry and Manufacture

Phosphate esters are produced by reaction of phosphoryl chloride with alcohols or phenols as shown in Eq. (6):



Early production of phosphate esters was based on the so-called crude cresylic acid fraction or tar acid derived by distillation of coal-tar residues. This feedstock is a complex mixture of cresols, xlenols, and other heavy materials and includes significant quantities of ortho-cresol. The presence of high concentrations of ortho-cresol results in an ester that has been associated with neurotoxic effects, and this has led to the use of controlled coal-tar fractions, in which the content of ortho-cresol and other ortho-*n*-alkylphenols is greatly reduced. Phosphate esters using coal-tar

fractions are generally referred to as “natural” as opposed to “synthetic” where high-purity raw materials are used.

The vast majority of modern phosphate esters are “synthetic,” using materials derived from petrochemical sources. For example, *t*-butylated phenols are produced from phenols by reaction with butylene. The reaction of alcohol or phenol with phosphoryl chloride yields the crude product, which is generally washed, distilled, dried, and decolorized to yield the finished product. Low-molecular-weight trialkyl esters are water-soluble, requiring the use of nonaqueous techniques. When mixed alkylaryl esters are produced, the reactant phenol and alcohol are added separately. The reaction is conducted in a stepwise process and the reaction temperature kept as low as possible to avoid transesterification reactions from taking place.

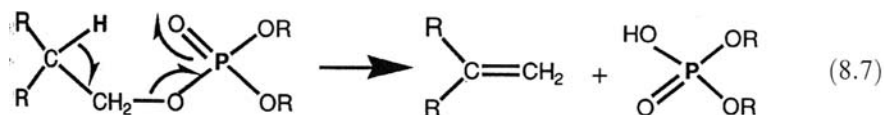
The most commonly used phosphate esters for antiwear performance features are tricresyl phosphates (TCP), trixylenyl phosphates (TXP), and tributylphenyl phosphates (TBP).

Physical and Chemical Properties

The physical properties of phosphate esters vary considerably according to the mix and type of organic substituents, the molecular weights, and structural symmetry, all proving to be particularly significant. Consequently, phosphate esters range from low-viscosity, water-soluble liquids, to insoluble high-melting solids.

As mentioned previously, the use of phosphate esters as synthetic base fluids arises mostly from their excellent fire resistance and superior lubricity but is limited due to their hydrolytic and thermal stability, low-temperature properties, and viscosity index. While phosphate esters are widely used as antiwear additives for lubricants, the concerns about hydrolytic stability, thermal stability, and, of course, satisfactory antiwear properties are equally important. In that sense, triaryl phosphates are dominant over trialkyl phosphates, because their hydrolytic-thermal stability is much better.

The thermal stability of triaryl phosphates is considerably superior to that of the trialkyl esters, which degrade thermally by a mechanism analogous to that of the carboxylic esters [Eq. (7)]:



With respect to hydrolytic stability, aryl phosphate esters are superior to the alkyl esters. Increasing chain length and degree of branching of the alkyl group lead to considerable improvement in hydrolytic stability. However, the more sterically hindered the substituent, the more difficult it is to prepare the ester. Alkylaryl phosphates tend to be more susceptible to hydrolysis than the triaryl or trialkyl esters.

The low-temperature properties of phosphate esters containing one or more alkyl substituents tend to be reasonably good. Many triaryl phosphates are fairly high-melting-point solids, but an acceptable pour point can be achieved by using a mixture of aryl components. Coal-tar fractions, used to make “natural” phosphate esters, are already complex mixtures and give esters with satisfactory pour points.

Phosphate esters are very good solvents and are extremely aggressive toward paints and a wide range of plastics and rubbers. When selecting suitable gasket and seal materials for use with these esters, careful consideration is required. The solvency power of phosphate esters can be advantageous in that it makes them compatible with most other common additives and enables them to be used as carriers for other, less soluble additives to generate an additive slurry.

2.2.2 Phosphites

Phosphites are the main organo-phosphorus compounds used to control oxidative degradation of lubricants. They eliminate hydroperoxides, peroxy, and alkoxy radicals, retard the darkening of lubricants over time, and also limit photodegradation. In addition to their important role as antioxidants, phosphites are also found to be useful antiwear additives. Dialkyl hydrogen phosphites and diaryl hydrogen phosphites are neutral esters of phosphorous acid. These materials have two rapid equilibrating forms: the keto form, $(RO)_2P(=O)H$, and the acid form, $(RO)_2P-O-H$. Physical measurements indicate that they exist substantially in the keto form, associated in dimeric or trimeric groupings by hydrogen bonding. Trialkyl phosphites and triaryl phosphites are neutral trivalent phosphorus esters. These materials are clear, mobile liquids with characteristic odors.

Chemistry and Manufacture

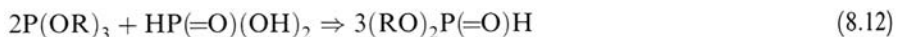
Phosphites are produced by reaction of phosphorus trichloride with alcohols or phenols as shown below:



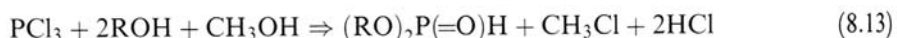
When mixed alkylaryl phosphites are produced, the reactant phenol and alcohol are added separately, with the reaction temperature carefully controlled. High-molecular-weight phosphites can be produced from transesterification reaction of either alcohols or phenols with trimethyl phosphite under catalytic (acidic) conditions.



With acid-catalyzed hydrolysis, dialkyl- or diaryl-hydrogen phosphites can be produced from trialkyl- or triaryl phosphites as shown below:



By carrying out the above reactions in the presence of hydrogen chloride acceptors such as pyridine, the isolation of mono-, di-, and trialkyl phosphites is feasible. However, with alcohols of normal reactivity, the product is often mainly dialkyl hydrogen phosphite. This can be made in up to 85% yield, by adding PCl_3 to a mixture of methanol and a higher alcohol at low temperature. The methyl and hydrogen chlorides are then removed by heating under reduced pressure on a steam bath.



The commonly used phosphites available in the marketplace are dimethyl hydrogen phosphite, diethyl hydrogen phosphite, diisopropyl hydrogen phosphite, dibutyl hydrogen phosphite, bis (2-ethylhexyl) hydrogen phosphite, dilauryl hydrogen phosphite, bis (tridecyl) hydrogen phosphite, dioleoyl hydrogen phosphite, trisnonyl-phenyl phosphite, triphenyl phosphite, triisopropyl phosphite, tributyl phosphite, triisooctyl phosphite, tris (2-ethylhexyl) phosphite, trilauryl phosphite, triisodecyl phosphite, diphenylisodecyl phosphite, diphenylisooctyl phosphite, phenyldiisodecyl phosphite, ethylhexyl diphenyl phosphite, and diisodecyl pentaerythritol diphosphite.

Chemical and Physical Properties

Phosphites tend to hydrolyze when exposed to humidity in the air or moisture in the lubricant. The extent of hydrolysis depends on the moisture content of the ambient atmosphere, the temperature, and the duration of exposure. Generally, liquid phosphites are more stable than solids because of the reduced surface area available for moisture pickup. But hydrolysis can be minimized if proper precautions, such as a dry nitrogen atmosphere, cool storage, and use of tight seals, are observed. The lower dialkyl hydrogen phosphites hydrolyze in both acidic and alkaline solutions to monoalkyl esters and phosphorous acid. Rates of hydrolysis normally decrease with increasing molecular weight. The lower esters of trialkyl phosphites are rapidly hydrolyzed by acids; however, they are relatively stable in neutral or alkaline solutions. In general, the hydrolytic stability of the trialkyl phosphites increases with molecular weight.

Since the dialkyl hydrogen phosphites are predominantly in the keto form, they are somewhat resistant to oxidation and do not complex with cuprous halides. Both of these reactions are characteristic of trivalent organic phosphorus compounds [21–23]. These esters are relatively resistant to reaction with oxygen and sulfur but react quite readily with chlorine and bromine, giving the corresponding dialkyl phosphorohalidates $[(RO)_2P(=O)X]$, where $X = Cl$ or Br [20].

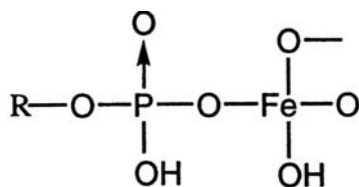
The hydrogen atom of the dialkyl hydrogen phosphites is replaceable by alkali but is not acidic in the usual sense. The alkali salts are readily obtainable by reaction of ester with metals. In contrast with the parent compound, these salts readily add sulfur to form the corresponding phosphorothioates. Sodium salts of phosphites can be reacted with alkyl chlorides to produce alkyl phosphonates. These salts react with halophosphites to produce pyrophosphites and with chlorine or bromine to yield the corresponding hypophosphates. Dialkyl hydrogen phosphites add readily to ketones, aldehydes, olefins, and anhydrides, and these reactions are catalyzed by bases and free radicals. This type of reaction provides an excellent method for preparing phosphonates.

Sulfur reacts readily with trialkyl or triaryl phosphites to form corresponding trialkyl or triaryl phosphorothioates, which are also very useful antiwear additives. The reaction of trialkyl phosphites with halogens is an excellent method for preparing dialkyl phosphorohalidates. Acyl halides and most polyfunctional primary aliphatic halides can be used. Triisopropyl phosphite provides a unique means for preparation of asymmetrical phosphonates and diphosphonates because the byproduct isopropyl halide reacts very slowly and thereby does not compete with the primary reaction.

Applications and Performance Characteristics

Dialkyl- (or diaryl-) hydrogen phosphites, besides being excellent antiwear agents, are considered the most potent form of phosphorus, suited to high-torque, low-speed operations. This is the area where antiwear processes are taken to the extreme and is one of the most important sections of the EP performance spectrum. Sulfur can be quite incapable of giving protection under such conditions. Only a phosphorus source, if active enough and in sufficient concentration, can help here. Conversely, phosphorus components are of little use in high-speed and shock operations where sulfur components can be excellent. Dialkyl or diaryl phosphites are also potent anti-oxidants.

With dialkyl phosphites, it has been reported that oxidation produces a phosphate anion that tends to act as a bridging ligand to form an oligomeric iron (III) complex, that is, an iron oxide complex resembling the following structure:



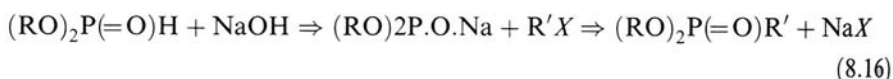
Structure C

However, there is also a weaker, high-viscosity, nonsolid film that increases the overall thickness of the total film at high speeds [18,24].

Dialkyl phosphites are widely used in gear oils, automatic-transmission fluids (ATF), and many other applications.

2.2.3 Dialkyl Alkyl Phosphonates

Dialkyl alkyl phosphonates $[\text{R}-\text{P}(=\text{O})(\text{OR})_2]$ are stable organic phosphorous compounds that are miscible with ether, alcohol, and most organic solvents. Besides being used as additives in solvents and low-temperature hydraulic fluids, they can also be used in heavy-metal extraction, in solvent separation, and as pre-ignition additives to gasoline, antifoam agents, plasticizers, and stabilizers. Dialkyl alkyl phosphonates are prepared from either dialkyl hydrogen phosphites or trialkyl phosphites as described below (Michaelis–Arbusov reaction):



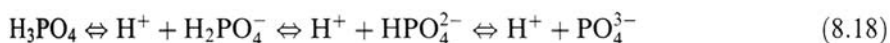
In principle, the thermal isomerization of all phosphites to phosphonates can be carried out. The stability of these compounds varies greatly; however, depending on the nature of the R group, other products may be formed during heating. For R = methyl, complete conversion occurs at 200°C in 18 hr, but for R = butyl,

the compound is stable at 223°C. Some researchers believe that isomerization of phosphites may be possible only if traces of phosphonate are already present as an impurity [25]:



2.2.4 Acid Phosphates

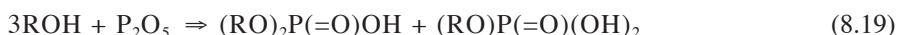
Acid phosphates are also potent additives, useful in similar areas of antiwear and EP to the dialkyl phosphites. Orthophosphoric (monophosphoric) acid (H_3PO_4), the simplest oxyacid of phosphorus, can be made by reacting phosphorus pentoxide with water. It is widely used in fertilizer manufacture. Orthophosphoric acid has only one strongly ionizing hydrogen atom and dissociates according to the following scheme:



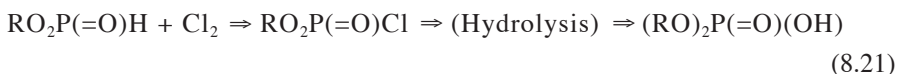
Since the first dissociation constant, K_1 (7.1×10^{-3}), is much larger than the second ($K_2 = 6.3 \times 10^{-8}$), very little of the H_2PO_4^- produced in the first equilibrium goes on to dissociate according to the second equilibrium. Even less dissociates according to the third equilibrium since the third constant, K_3 , is very small ($K_3 = 4.4 \times 10^{-13}$). The acid gives rise to three series of salts containing these ions, e.g., NaH_2PO_4 , NaH_2PO_4 , and Na_3PO_4 .

Chemistry and Manufacture

Alkyl (aryl) acid phosphates are made from alcohol (phenol) and phosphorus pentoxide. In general, a mixture of monoalkyl (aryl) and dialkyl (aryl) phosphates is produced:



Pure mono- or dialkyl (aryl) phosphates can be synthesized through different reaction route as described below:



Properties, Performance Characteristics, and Applications

Phosphoric acids tend to hydrolyze further when exposed to humidity. The extent of hydrolysis depends on the moisture content of the ambient atmosphere and the duration of exposure. Wherever possible, phosphoric acids should be handled in a dry nitrogen atmosphere to prevent hydrolysis. Therefore, for applications where incidental moisture contact is inevitable, acid phosphates are not recommended.

Acid phosphates are used as rust inhibitors and antiwear additives. However, they are not as widely used as their amine neutralized derivatives, e.g., amine phosphates.

2.3 Sulfur-Phosphorus Additives

Sulfur-phosphorus additives are used to provide protection against moderate-to-high-pressure, metal-to-metal contacts in boundary lubrication and elasto-hydrodynamic lubrication (EHL). Metallic sulfur-phosphorus additives, such as zinc dithiophosphates (ZnDTP), are the most important antiwear/EP components used in engine oils. Ashless sulfur-phosphorus additives are used less extensively. The most commonly available S/P additives in the marketplace are based on chemistries of dithiophosphates, thiophosphates, and phosphorothioates. Other important applications of S/P compounds are in matches, insecticides, flotation agents, and vulcanization accelerators.

2.3.1 Ashless Dithiophosphates

Numerous patents were issued on the use of phosphorodithioic acid esters in lubricating oils in the early days. U.S. Patent 2,528,732 describes alkyl esters of phosphorodithioic acid. U.S. Patent 2,665,295 describes the S-terpene ester, while U.S. Patent 2,976,308 describes an anti-Markovniko addition of phosphorodithioic acid ester to various olefins, both aromatic and aliphatic. Amine dithiophosphates and other novel dithiophosphate esters are reported in the literature [26-30]. Coupling with vinyl pyrrolidinone, acrolein, or alkylene oxides (to make hydroxyl derivatives) is also known [31-33].

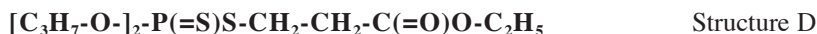
Chemistry and Manufacture

Similar to metallic dithiophosphates, ashless dithiophosphates are also based on phosphorus pentasulfide (P_2S_5) chemistry. They can be prepared from the same precursor of ZnDTP, dithiophosphoric acid [Eq. (22)] through the reaction of alcohol (or alkylphenol) and P_2S_5 .



The dithiophosphoric acids are further reacted with an organic substrate to generate ashless derivatives. Typical organic substrates are compounds such as olefins, dienes, unsaturated esters (acrylates, methacrylates, vinyl esters, etc.), unsaturated acids, and ethers. The efficiency and stability of the ashless dithiophosphates very much depend on components used in their manufacture and the reaction conditions.

The most common ashless dithiophosphate used in the marketplace is a dithiophosphate ester made from ethyl acrylate and o, o-diisopropyl dithiophosphoric acid as described below:



Treatment, of terpenes, polyisobutylene (PIB), or polypropylene (PP) with phosphorus pentasulfide and hydrolysis give thiophosphonic acids $[R-P(=S)(OH)_2]$, where R = PIB, terpenes, or PP). They can be further reacted with propylene oxide or amines to reduce acidity. However, this type of additive belongs to the same class of chemicals called ashless dispersants. Hence, they can be dual functional dispersants with improved antiwear/EP properties.

Applications and Performance Characteristics

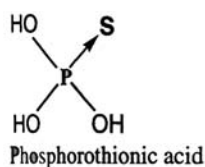
Unlike ZnDTP, ashless dithiophosphates are usually not as versatile and therefore can not be considered multifunctional additives. Although ashless dithiophosphates

have fairly good antiwear and EP properties, their anticorrosion properties are not as good as ZnDTP. This is closely related to the stability and decomposition mechanisms of ashless dithiophosphates. Relatively weak corrosion protection also limits their application at high concentrations in engine oils as well as some industrial oils.

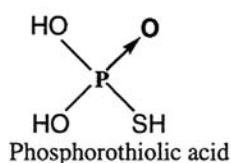
Ashless dithiophosphates can be useful in metal-working fluids, automotive-transmission fluids (ATF), gear oils, greases, and nonzinc hydraulic fluids.

2.3.2 Ashless Phosphorothioates and Thiophosphates

Numerous esters of the phosphorothioic acids are known. In salts and esters of these oxygen/sulfur (O-S) acids there may be a preferred location of the multiple bond, but in general this is not well known. Thus, in principle, there are two series of possible acids, each of which might give rise to salts and esters as described below:



(Thionophosphoric)

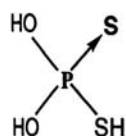


(Thiolophosphoric)



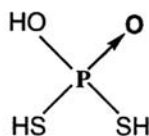
Phosphorothioic acid

(Thiophosphoric)



Phosphorothiolothionic acid

(Thiolothionophosphoric)



Phosphorodithiolic acid

(Dithiolophosphoric)



Phosphorodithioic acid

(Dithiophosphoric)

The “thionic” acids contain the group $\text{P}=\text{S}$, while the “thiolic” acids contain the group $\text{P}-\text{SH}$. The term “thioic” is often used when the molecular form is unknown or when specification is not desired. One form of these acids is usually more stable than the other, and it may not be possible to prepare both esters as, for instance, the isomers of phosphorothioic acid:

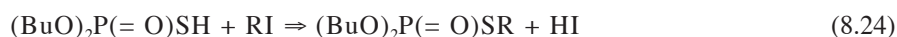


In the case of some esters, the thio form is the most stable, but the phenyl ester exists 80% in thiono, $(\text{PhO})_2\text{P}(=\text{S})\text{OH}$, and 20% in thiolo, $(\text{PhO})_2\text{P}(=\text{O})\text{SH}$, forms. The equilibrium of these compounds is liable to depend on the nature of the R

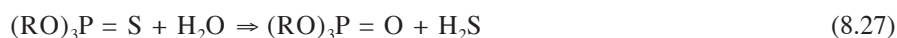
groups, the solvent used, and even the concentration. Intermolecular hydrogen bonding may be expected to play a part in such equilibrium [25].

Chemistry and Manufacture

The creation of a compound with a phosphorus-sulfur linkage can often be carried out simply by heating the appropriate phosphorus compound with sulfur [34]. Likewise, the replacement of oxygen by sulfur in compounds containing P-O linkages can also be achieved simply by heating them with P_2S_5 . Inorganic phosphorothioates (thiophosphates) are usually prepared from sulfur-containing phosphorus compounds. They are produced during the hydrolytic breakdown of phosphorus sulfides and are often unstable in water. They hydrolyze to the corresponding oxy compounds with the evolution of H_2S . Phosphorus-sulfur compounds are often thermally less stable than their oxy analogs. A few examples are listed as follows:



Hydrolysis of phosphorothioate esters results in a progressive loss of sulfur as hydrogen sulfide (H_2S) and its replacement by oxygen.



2.3.3 Applications and Performance Characteristics

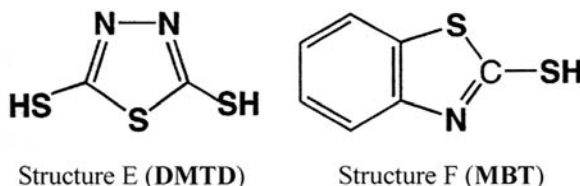
It has been known for many years that sulfur compounds form a film of iron sulfide, and phosphorus compounds form iron phosphate, on the mating metal surfaces. Generally, the films formed from sulfur sources such as SIB are expected to contain FeS , $FeSO_4$, as well as organic fragments from the additive decomposition. With phosphorus sources, such as dialkyl phosphites, films containing $FePO_4$, $FePO_3$, as well as organic fragments are expected. When both sulfur and phosphorus are present, both elements contribute to the nature of the film, and which one predominates depends on the S/P ratio, the decomposition mechanisms, and the operating conditions, for example, high speed and shock or high torque/low speed.

Ashless phosphorothioates are widely used as replacements for metallic dithiophosphates in many lubricant applications where metal is less desirable. Phosphorothioates are often present (generated in situ) in lubricant formulations when both sulfur and phosphorus additives are used. Aryl phosphorothioates provide good thermal stability and good antiwear/EP properties as evidenced by their strong FZG performance.

2.4 Sulfur-Nitrogen Additives

Sulfur- and nitrogen-containing additives are used to provide protection against moderate- to high-pressure, metal-to-metal contacts in boundary lubrication and elastohydrodynamic lubrication. Both open-chain and heterocyclic compounds have attracted a considerable amount of research effort to explore their potential as

antiwear and EP additives. Among open-chain additives, dithiocarbamates are the most widely used. Other additives, such as organic sulfonic acid ammonium salts [35], and alkyl amine salts of thiocyanic acid [36] are reported in the literature but are of relatively low commercial value. Nitrogen- and sulfur-containing heterocyclic compounds, such as 2-mercaptobenzothiazole (MBT), 2,5-dimercapto-1, 3, 4-thiadiazole (DMTD), and their derivatives, have been used for many years as antioxidants, corrosion inhibitors, and metal passivators, generally at relatively low concentrations.

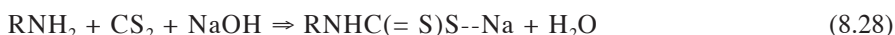


2.4.1 Dithiocarbamates

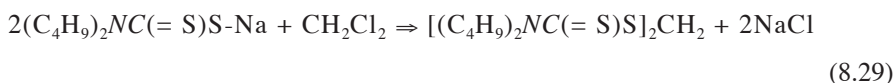
The dithiocarbamates, the half-amides of dithiocarbonic acid, were discovered as a class of chemical compounds early in the history of organo-sulfur chemistry [37,38]. The strong metal-binding properties of the dithiocarbamates were recognized early, by virtue of the insolubility of the metal salts and the capacity of the molecules to form chelate complexes. Other than applications in lubricant areas, dithiocarbamates have been used in the field of rubber chemistry as vulcanization accelerators and antiozonants.

Chemistry and Manufacture

Organic dithiocarbamates can be made by a one-step reaction of dialkylamine, carbon disulfide, and an organic substrate. The organic substrate is preferably an olefin, diene, epoxide, or any other unsaturated compounds exemplified in the literature [39,40]. Organic dithiocarbamates can also be made through a two-step reaction involving ammonium or metal dithiocarbamate salts and organic halides [41]. In the case of their ammonium salts, N-substituted dithiocarbamic acids, RNHC(=S)SH or $\text{R}_2\text{NC(=S)SH}$, are formed by reaction of carbon disulfide with a primary or secondary amine in alcoholic or aqueous solution before they are further reacted with ammonia. In order to conserve the more valuable amine, it is common practice to use an alkali-metal hydroxide to form the salt:



The dithiocarbamic acid can be precipitated from an aqueous solution of dithiocarbamate by adding strong mineral acid. The acids are quite unstable but can be held below 5°C for a short time. The most common additive, methylene bis-dibutyl dithiocarbamate, is prepared from sodium dibutyl dithiocarbamate and methylene chloride:



Applications and Performance Characteristics

Unlike metallic dithiocarbamates, which have been widely used in lubricants, ashless dithiocarbamates have been gaining attention only recently. Their relatively high

cost certainly is a major factor in limiting wider use. The success of metallic dithiocarbamates also overshadows their ashless counterpart. Certain metallic dithiocarbamates, such as molybdenum dithiocarbamates, offer exceptionally good frictional properties that also cannot be matched by their ashless analogs. However, ashless dithiocarbamates have been found to be versatile, multifunctional additives in a few areas. They can be effective antiwear/EP additives, as well as good antioxidants and metal deactivators. They tend to generate less sludge or deposits than mostly metallic additives, and they are very compatible with various base oils.

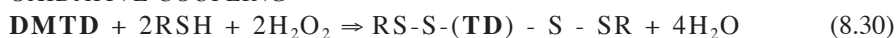
2.4.2 Dimercaptothiadiazole and Mercaptobenzothiazole Additives

Additives derived from 2,5-dimercapto-1,3,4-thiadiazole (DMTD) and 2-mercaptobenzothiazole (MBT) are well documented in the literature. Due to strong ring stability (partial aromaticity and resonance delocalization), balanced sulfur-nitrogen distributions, and reactive mercaptan groups, both heterocyclic compounds can be versatile core molecules to make many useful additives with many beneficial characteristics, such as improved thermal/oxidative stability and reduced corrosivity. Unfortunately, some potentially good reactions are hampered by the limited solubility of DMTD and MBT in common petrochemical solvents. Therefore, a suitable sample preparation procedure is very critical to help achieve desirable antiwear/EP additives.

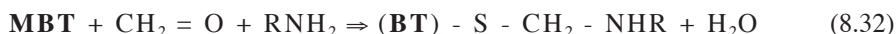
Chemistry and Manufacture

Many differing organic reactions can be applied to functionalize the mercaptan groups of DMTD and MBT. Oxidative coupling reactions involving other alkyl mercaptans can bring in additional sulfur for EP performance and additional alkyl chains for improved solubility [42]. Addition reactions with organic compounds containing activated double bonds can link DMTD or MBT heterocyclic core molecules with long-chain esters, ketones, ethers, amides and acids together [43-46]. Likewise, ring opening with epoxides to generate alcohol derivatives is also known [47]. Direct amine salts formation and linking alkyl amines through Mannich base condensation are also extensively studied [48-50]. A number of examples are listed below, where TD is the abbreviation for the thiadiazole moiety and BT is for the benzothiazole moiety.

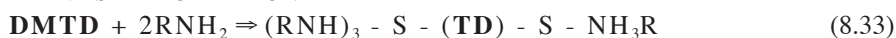
OXIDATIVE COUPLING



MERCAPTO ALKYLATION AND MANNICH ALKYLATION



AMINE SALT FORMATION



Applications and Performance Characteristics

MBT is a light yellow powder with limited solubility in hydrocarbons. It is more soluble in aromatic solvent (~1.5% in toluene), polar solvents, and, highly aromatic oils. MBT is used as a copper corrosion inhibitor in fuels as well as a corrosion inhibitor/deactivator in numerous industrial lubricants such as heavy-duty cutting and metal-working fluids, hydraulic oils, and lubricating greases. DMTD is also a light yellow powder with very limited solubility in hydrocarbons. It is considered a versatile chemical intermediate suitable for making various oil-soluble derivatives.

Both MBT and DMTD derivatives are widely used as copper passivators and nonferrous metal corrosion inhibitors. Some proprietary load-carrying additives are substituted MBT and DMTD compounds that are used in various applications either as a component or a part of additive packages with a specific purpose. In the absence of any phosphorus moiety in MBT and DMTD, their oil-soluble derivatives are suitable for replacing zinc dithiophosphates in some lubricant applications. VanlubeTM 829 (R. T. Vanderbilt Company), a high-density, powderlike DMTD derivative is used as a dual functional antioxidant/extreme-pressure agent in greases.

2.4.3 Other Sulfur-Nitrogen Additives

In addition to DMTD, MBT, and dithiocarbamate additives, other sulfur-nitrogen-containing additives are available in the marketplace or reported in the literature. Among these, thiuram monosulfides, thiuram disulfides, and benzoxazoles are of particular interest because they are all sulfur-and nitrogen-rich molecules. Thiuram disulfides, chemically similar to dithiocarbamates, can be used in the rubber industry as vulcanizers. 2-Alkyldithio-benzoxazoles also offer good frictional properties in addition to strong antiwear/EP properties [51].

2.5 Phosphorus-Nitrogen Additives

Phosphorus-nitrogen additives are used to provide protection against moderate-to high-pressure, metal-to-metal contacts in boundary lubrication and elasto-hydrodynamic lubrication. Ashless phosphorus-nitrogen additives are used as dual functional antiwear/antirust additives extensively, and the most commonly available in the marketplace are based on chemistries of amine dithiophosphates, amine thiophosphates, amine phosphates, and phosphoramides.

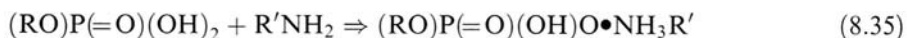
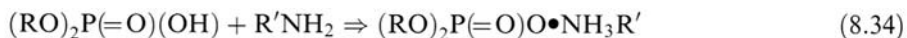
2.5.1 Amine Phosphates

Amine phosphates are by far the most important phosphorus-nitrogen-containing additives used in lubricants. In fact, they are multifunctional additives possessing very good antirust as well as antiwear/EP properties.

Chemistry and Manufacture

Amine phosphates are produced by treating acid phosphates with alkyl or aryl amines. Under various conditions, neutral, overbased, and underbased amine phosphates can be synthesized. If mixed mono- and di-alkyl acid phosphates are used as starting materials, mixed mono- and di-alkyl amine phosphates are produced. The final additives usually possess high total acid number (TAN) and high total base

number (TBN), although reaction adducts are considered fairly neutral. It is known that a complete neutralization of both phosphoric acid groups in monoalkyl acid phosphates with amines cannot be easily achieved, and therefore, under normal conditions, a partially neutralized amine phosphate is formed.



Applications and Performance Characteristics

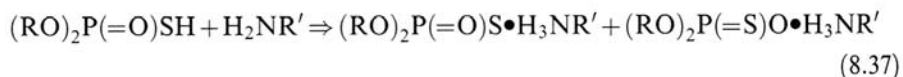
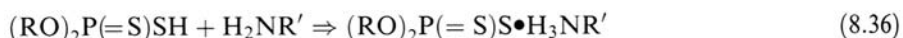
Amine phosphates are extensively used in industrial oils, greases, and automotive gear oils. They offer very good rust protection as demonstrated in various bench rust tests (ASTM D665 and CRC L-33). They also show very good antiwear/EP characteristics (four-ball wear and four-ball EP, FZG, Timken and CRC L-37). Since amine phosphates are very polar species, they interact strongly with other additive components, making their performance very dependent on the formulation. Hence, extra attention is needed when amine phosphates are used.

2.5.2 AmineThiophosphates and Dithiophosphates

Amine thiophosphates and amine dithiophosphates can be found in engine oils and industrial oils where zinc dithiophosphates and other nitrogen-containing additives are used, either as decomposition products or in situ produced products. They are critical to the lubricant performance because of their high activity toward metal surfaces.

Chemistry and Manufacture

Amine thiophosphates are produced by reacting thiophosphoric acid with alkyl or aryl amines [52]. Likewise, amine dithiophosphates are synthesized from dithiophosphoric acid and amines.



Applications and Performance Characteristics

Amine thiophosphates and dithiophosphates are also multifunctional additives providing good rust inhibition and antiwear properties. Due to their high activity and low stability, amine thiophosphates and dithiophosphates are not as extensively used as either amine phosphates or metallic dithiophosphates. A detailed study of their antiwear mechanisms suggested that a tribo-fragmentation process is involved [53]. Relatively poor corrosion control is one area of concern that needs attention. With proper formulation adjustments, it is quite feasible to overcome certain intrinsic weaknesses and apply both chemistries to various lubricant products.

2.5.3 Other Phosphorus-Nitrogen Additives

Many other phosphorus/nitrogen-containing ashless antiwear additives are reported in the literature. Some are proprietary technologies, and their commercial status is unknown. Organophosphorus derivatives of benzotriazole are a group of additives

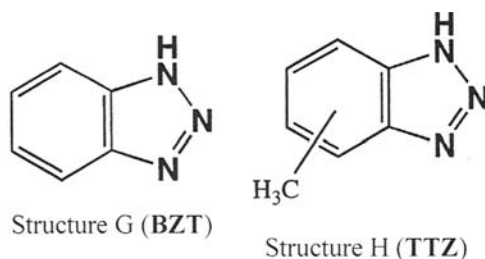
based on triazole and di-alkyl or di-alkylphenyl phosphorochloridate chemistry [54]. Arylamines and dialkyl phosphites can be coupled through a Mannich condensation reaction to form unique phosphonates that are used as multifunctional antioxidant and antiwear additives [55]. Bisphosphoramides are also reported [56].

2.6 Nitrogen Additives

Nitrogen-containing additives are used to provide rust inhibition and cleanliness features in various lubricant applications. For example, nitrogen-containing ashless dispersants are a key component for engine oils, and alkoxyated amine compounds are used in lubricating greases to provide corrosion inhibition [57]. Furthermore, arylamines are widely used as antioxidants due to their abilities to terminate radical chain propagation and decompose peroxides. Very few nitrogen additives alone are considered effective antiwear/EP additives, and their performance is either very specific to industrial applications or fairly dependent on product formulations. However, when used in combination with other sulfur, phosphorus, or boron additives, nitrogen-containing additives can be very effective supplements to enhance antiwear/EP performance.

Chemistry, Manufacture, and Performance

Several novel chemistries are available in the literature for nitrogen-only antiwear additives. Among these, dicyano compounds were tested and exhibited very good four-ball wear activities [58]. Polyimide-amine salts of styrene-maleic anhydride copolymers are also reported as antiwear additives; however, high additive concentrations (5–10%) are needed [59]. Products of nitrogen heterocycles, such as benzo-triazole (BZT) and tolyltriazole (TTZ) (Structures F and G) with amines or carboxylic acids, have been found to be effective antiwear additives in both lubricants and fuels [60–62]. Although triazoles are costly chemicals, they have unique geometric structures that contribute high surface-film-forming efficiency.



Both BZT and TTZ derivatives are also effective copper deactivators at low concentrations. Therefore, these types of additives are indeed dual functional. They find applications in industrial oils, greases, and fuels.

2.7 Halogen Additives

Chlorine was one of the earliest antiwear and EP elements used in the lubricant industry. Chlorine-containing additives are still used in cutting oils and related

metal-working lubricants, in combination with sulfur additives. Iodine was mentioned in aluminum-processing lubricants for wear control. Fluorine, in perfluorinated compounds, is well known to reduce wear and especially friction.

The chlorine compounds act and function in that they coat the metal surface with a metal chloride film under the influence of the high pressure at the point of lubrication and in the presence of traces of moisture. FeCl_2 melts at 672°C and has low shear strength in comparison with steel.

The effect of the chlorine compounds depends on the reactivity of the chlorine atom, the temperature, and the concentration. Hydrogen chloride formed in the presence of larger quantities of moisture can cause severe corrosion of the metal surfaces. As the corrosion hazards increase along with the EP properties with increasing reactivity of the chlorine atoms, a compromise must be found in the development of chlorine-containing additives.

Chlorinated paraffins such as trichloroacetane represent a group of important EP additives used in the past. They can significantly increase the load stages in the FZG test with increasing concentration. The chain length has practically very little influence on the EP effect; on the other hand, the load-carrying capacity increase with increasing degree of chlorination. In practice, chlorinated paraffins with ~40 to 70 wt% chlorine are used; however, they are sensitive to moisture and light and can easily evolve into hydrogen chloride [63]. Compounds such as phenoxy-propylene oxide, amines, or basic sulfonates neutralize the hydrogen chloride and thus act as stabilizers.

Good results are also obtained with chlorinated fatty acids and their derivatives, particularly those with trichloromethyl groups in the end position, since the additives with $-\text{CCl}_3$ groups are particularly effective.

Due to their high stability, chlorinated aromatics have less favorable EP properties than the chlorinated aliphatics. Alkylaromatics with chlorinated side chains improve the load-carrying capacity much more than those chlorinated in the ring; the efficiency increases with the number of carbon atoms in the side chain. Chlorinated fatty oils and esters as well as chlorinated terpenes and amines have also been patented as EP additives.

Sulfur-chlorine additives were found to be satisfactory for gear lubrication in passenger cars in the mid-1930s. Apparently, this type of additive could satisfy the high-speed and moderate load operation of passenger cars used at that time. When sulfur and chlorine are combined in the organic molecule, the sulfur somewhat reduces the corrosive tendency of chlorine; on the other hand, the EP properties of the combined moieties are improved in comparison with the individual compounds. Chlorinated alkyl sulfides, sulfurized chlorophthalenes, chlorinated alkyl thiocarbonates, bis-(p-chlorobenzyl) disulfide, tetrachlorodiphenyl sulfide, and trichloroacrolein mercaptals $[\text{Cl}_2\text{C}=\text{CCl}-\text{CH}(\text{SR}')-\text{SR}'']$, where R' and R'' are alkyl or aryl] must be mentioned in this class. Reaction products of olefins and unsaturated fatty acid esters with sulfur chlorides contain highly reactive β -chlorosulfides, which due to their reactive chlorine and sulfur atoms give very good EP agents yet show more or less strong corrosive tendencies. However, severe wear was frequently encountered in truck axles, where performance under high-torque, low-speed conditions is of greater importance. Later on, the presence of chlorine, although a good EP agent, was found to be detrimental to lubricant thermal stability. Hence, for the last 30 years, chlorine has not been used in gear oils.

Chlorinated trioleyl phosphate, condensation products of chlorinated fatty oils with alkali salts of dithiophosphoric acid diesters, and reaction products of glycols with PCl_3 are examples of chlorine-phosphorus additives used in earlier years.

The most serious drawback for chlorine antiwear and EP additives is in the environmental area. Legislation around the industrial world limits the chlorine content of many lubricants to parts per million. Therefore, except for the cutting oil industry, which is also under pressure to change, Chlorine additives are not considered a viable option for modern lubricants.

2.8 Nontraditional Antiwear/EP Additives

Traditional sulfur-, phosphorus-, and halogen-related compounds are considered to be the dominant antiwear/EP additives in the marketplace. However, as environmental concerns escalates, the future trends will favor products that diminish potential hazard and disposal problems. Recent clean fuel activities are driving sulfur levels toward 10–50 weight parts per million ranges. Subsequently, the petroleum industry is favoring lower sulfur lubricants since sulfur is also known to poison the catalytic system used for NO_x reduction. Therefore, the use and development of nontraditional antiwear additives are becoming more valuable.

Several nonsulfur, nonphosphorus ashless antiwear additive technologies are reported in the literature [64,65]. Among these, high hydroxyl esters (HHE), dimer acids, hydroxylamine esters, acid anhydrides, cyclic amides, and boron derivatives are recognized as leading technologies. Graphite and TeflonTM possess excellent friction reduction properties and indirectly contribute some antiwear/EP characteristics. However, both materials have very limited lubricant solubility, which hampers their usefulness. Organic borates are considered effective friction modifiers, antioxidants, and cleanliness agents. Recent studies indicate that some borates can be good antiwear additives. Chevron's potassium borates have been used in gear oils for years, but these types of metallic borates are outside the scope of this chapter. Esters are known to possess good lubricity properties. The properties can be further improved to offer antiwear characteristics through proper functionalization. Companies like ExxonMobil Chemical and Lubrizol (formerly Gateway Additives) all have marketable products in this area.

3 MANUFACTURE, MARKETING, AND ECONOMICS

All major additive suppliers produce ashless antiwear and EP additives that are available as components and as packages. A list of common producers is summarized in [Table 2](#).

Ashless antiwear and EP additives are supplied in a variety of chemistries, including single and multiple blends formulated to maximize performance and minimize adverse effects (e.g., dropout, corrosion, etc.). Product designations vary by chemical class and concentration. Many of them are formulated into additive packages according to applications, such as passenger car engine oils, heavy diesel engine oils, automotive transmission oils, automotive gear oils, hydraulic fluids, and others. Examples of ashless antiwear and EP additives by selected suppliers are illustrated in [Table 3](#).

Table 2 Common Producers of Ashless Antiwear/EP Additives

Infineum	Lubrizol	Ethyl
Oronite (Chevron)	Ciba Specialty Chemicals	R. T. Vanderbilt
Elco (Detrex)	Mayco (BP-Amoco-Castrol)	Keil Chemical Div. (Ferro)
Crompton	FMC	AtoFina
Rhein Chemie	Clariant	GE Specialty Chemicals
Great Lake Chemicals	Dow (formerly Angus)	Polartech
Uniqema (ICI)	Akzo Nobel	Zeneca
Rhodia (Albright & Wilson)	BASF	Dover Chemical

There has been some consolidation in the additive business, but the market has not changed much as a result. In 1997 Lubrizol bought Gateway Additives (Spartanburg, SC) and in 1999 Crompton completed a merger with Witco. The largest merger in lubricant additives is the formation of Infineum from Exxon Chemical's Paramins and Shell Chemical Additives. Since most lubricant additives are produced through batch processes, consolidation can help improve operations and lower costs (e.g., reducing plant idle time with better chemical manufacturing management systems). Many manufacturing facilities still use equipment and procedures that are 30–40 years old. Hence, any investments in automation and continuous processing for the plant will be a competitive advantage. However, the business is so flat that most suppliers have difficulties in justifying capital expansion.

4 EVALUATION EQUIPMENT/SPECIFICATION

4.1 Lubricant Specifications

Lubricant components and formulated products are manufactured to tight specifications in petroleum refineries and lubricant blending plants and must also meet detailed commercial, industrial, and military specifications. As an example, the U.S. Military has rigid specifications for automotive lubricants, while the automotive manufacturers have similarly rigid, but not necessarily the same specifications, to ensure quality and consistency of lubricant manufacture. In addition, performance specifications that must be met from such original equipment manufacturers (OEMs) as farm machinery and other off-highway automotive equipment exist. These

Table 3 Ashless Antiwear/EP Additives

Supplier	Designation	Chemical class
Lubrizol	Anglamol 33	sulfurized isobutylene
Ethyl	Hitec 2375	S/P gear oil additive package
Ciba	Irgalube 63	Ashless dithiophosphates
Elco	Elco-301	Chlorinated paraffins
Keil	CW-35	Chlorinated paraffins
AtoFina	TPS-37	Dialkyl pentasulfides
R. T. Vanderbilt	Vanlube7723	Ashless dithiocarbamates

specifications are designed to enable the user to select appropriate lubricants and to be assured of adequate performance over a specified service life.

The industry is, for the most part, adequately self-regulating with minimal government input concerning performance specifications. The most elaborate system for developing and upgrading lubricant and fuel specifications is for automotive lubricants. The American Society of Testing and Materials (ASTM), the Society of Automotive Engineers (SAE), and the American Petroleum Institute (API) all have defined roles in determining specifications for products such as passenger car motor oils and heavy-duty motor oils. These three organizations, working together in the United States, are known as the Tripartite. Extending internationally, the International Lubricant Standardization and Approval Committee (ILSAC) is also active in all phases of engine lubricant category development.

In other product categories, lubricant and additive suppliers, OEMs, and industry trade associations work together to determine performance requirements and product specifications. In addition to the three industry organizations mentioned above, the National Lubricating Grease Institute (NLGI), the National Marine Manufacturers Association (NMMA), the American Gear Manufacturers Association (AGMA), the Society of Tribologists and Lubrication Engineers (STLE), and other groups, associations, and key equipment builders can influence lubricant specifications.

In addition to meeting all military and industrial specifications, many leading lubricant marketers and finished lubricant supplies develop their own internal specifications to be used for new-product launching, competitive product analysis, and future-product development. Proprietary field testing is an integral part of the overall new lubricant product development processes and often is the most critical step to assure technical success and customer satisfaction for new products.

4.2 Additive Specifications

Specifications for antiwear/EP additives focus primarily on application, base oil compatibility, and quantification of elemental constituents. In addition, specifications typically identify specific and critical performance standards for applications. Common specifications for antiwear/EP additives are shown in [Table 4](#).

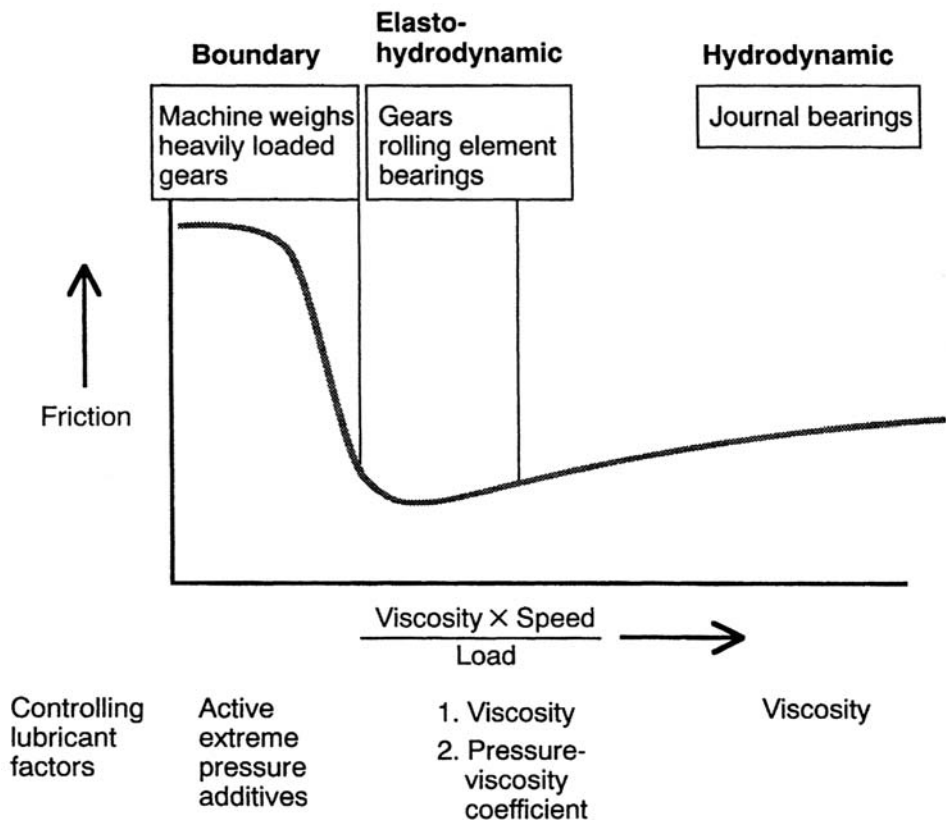
In addition to typical specifications as reported in the Certificate of Analysis (C of A) from additive suppliers, individual lubricant marketers often prefer to conduct their own internal additive specifications, such as infrared analysis and key performance testing.

4.3 Test Methods and Equipment

In the United States a number of bench and advanced tests were developed and approved by the ASTM. These tests have gained widespread reception throughout the industry. However, a few selected lab bench and advanced tests developed and approved only by specific original equipment manufacturers but represent certain critical and desirable performance features ([Figure 2](#), lubrication regimes). This chapter is not intended to cover all evaluation tests in detail, but rather to illustrate a few representative tests to highlight the key assessment criteria.

Table 4 Typical Specifications for Antiwear and EP Additives

Chemical class	Property	Performance test
Amine phosphates	%nitrogen, phosphorus, and TAN/TBN	Four-ball wear, four-ball EP, FZG, rust/oxidation test
methylene bis-dialkyl dithiocarbamate	%Sulfur, nitrogen, and residual chlorine, amine	Four-ball EP, FZG, Falex EP, oxidation/corrosion test
Sulfurized lard, esters, fatty acids	%total sulfur; %active sulfur	Four-ball wear, four-ball EP, stick-slip, Cu corrosion
Triphenyl phosphorothioate	%Sulfur, phosphorus, and melting point	Four-ball EP, FZG, Falex EP, oxidation/corrosion test
Chlorinated paraffins, fatty acids	%Chlorine, acid value	Four-ball wear, Falex EP, Timken, Cu corrosion

**Figure 2** Lubrication regimes.

Four-Ball Wear and EP Test

This tester was developed to evaluate the antiwear, EP, and antiweld properties of lubricants. It is a simple bench test machine designed to measure the protection a lubricant provides under conditions of high unit pressures and various sliding velocities. The four-ball wear tester consists of four 1/2-in.-diameter steel balls arranged in the form of an equilateral tetrahedron. The three lower balls are held immovably in a clamping pot, while the fourth ball is caused to rotate against them. Test lubricant is added in the test pot, covering the contact area of the test balls. During a test, wear scars are formed on the surfaces of the three stationary balls. The diameter of the scars depends on the load, speed, temperature, duration of run, and type of lubricant. The four-ball EP tester runs at a fixed speed of 1770 ± 60 rpm and has no provision for lubricant temperature control. A microscope is used to measure the wear scars. Two of the standard tests run on the four-ball machine are mean-hertz load and load-wear index. ASTM D 2596 covers the detailed calculation procedure of load-wear index for greases and D-2783 for oils. These procedures involve running a series of 10-sec tests over a range of increasing loads until welding occurs. From the scar measurements, the mean load (load-wear index) is calculated and serves as an indicator of the load-carrying properties of the oil tested.

FZG Four-Square Gear Test Rig

The FZG test equipment consists of two gear sets, arranged in a four-square configuration, driven by an electric motor. The test gear set is run in the test fluid, while increasing load stages (from 1 to 13) until failure. Each load stage is run for a 15-min period at a fixed speed. Two methods are used for determining the damage load stage. The visual rating method defines the damage load stage as the stage at which more than 20% of the load-carrying flank area of the pinion is damaged by scratches or scuffing. The weight loss method defines the damage load stage as the stage at which the combined weight loss of the drive wheel and pinion exceeds the average of the weight changes in the previous load stages by more than 10 mg. The test is used in developing industrial gear lubricants, automatic-transmission fluids, and hydraulic fluids to meet various manufacturers' specifications.

Falex EP/Wear Tester

The Falex test machine provides a rapid method of measuring the load-carrying capacity and wear properties of lubricants. The test consists of rotating a test pin between two loaded journals (V-blocks) immersed in the lubricant sample. Two common tests are run in this machine: one is an EP test (subjecting a test lubricant to increasing loads until a failure occurs), and the other is a wear test (subjecting a lubricant to a constant load for a definite period of time while measuring the wear pattern).

Timken EP Test

The Timken EP test provides a rapid method of measuring abrasion resistance and the load-carrying capacity of lubricants. A number of lubricant specifications require Timken "OK" loads above certain minimum values. The mode of operation consists of rotating a Timken tapered roller bearing cup against a stationary, hardened steel

block. Fixed weights force the block into contact with the rotating cup through a lever system. The OK load is the highest load the cup and block will carry without scoring during a 10-min run. Timken abrasion tests are run under fixed loads for extended time periods, and the weight loss of the cup and block are a measure of the abrasion resistance of the lubricant.

L-37 High-Torque Test

The CRC L-37 test operates under low-speed, high-torque conditions. It evaluates the load-carrying ability, wear stability, and corrosion characteristics of gear lubricants. The test differential is a Dana Model unit driven by a Chevrolet truck engine and four-speed transmission. A complete, new axle assembly is used for each test after a careful examination of gear tooth and bearing tolerance. After break-in at reduced load and high speed, the test continues for 24hr under low-speed (80 axle rpm) and high-torque conditions.

L-42 High-Speed Shock Test

The CRC L-42 test is established to evaluate the antiscoring performance of EP additives in gear lubricants under high-speed, shock load conditions. The test axle is a Dana Model unit driven by a Chevrolet engine through a four-speed truck transmission. The procedure requires five accelerations in fourth gear with inertia loading, and ten accelerations in third gear with dynamometer loading. The lubricant evaluation is based on the amount of scoring, and test results are expressed as percent tooth contact area scored.

FAG FE-8 Test

FAG developed this test frame to be a flexible “tribological” system to conduct tests over a wide range of operating conditions with different test bearings. Short-duration standardized tests have been developed for different applications. FAG also uses longer term testing (e.g., fatigue) for comprehensive evaluations. The FE-8 gear oil test was developed specifically to evaluate the effectiveness of antiwear additives. The test runs under heavy load and low speed that forces the bearing to operate under boundary lubrication conditions.

GEAR TEST CONDITIONS

Bearings:	Cylindrical roller/thrust loaded
Speed:	7.5 rpm
Load:	114 kilo-Newtons
Bearing temperature:	Variable
Test duration:	80 hr

Other tests including Optimol SRV, Cameron-Plint, Falex Multi-Specimen, Vickers Vane pump, Vickers 35-VQ-25 pump, and Denison high-pressure pump tests are also used widely in evaluation of various lubricants and greases. Appropriate field tests are also arranged in proprietary test sites to ensure good product quality and equipment compatibility/friendliness prior to new-product introduction to the marketplace.

On the engine oil side, the International Lubricant Standardization and Approval Committee (ILSAC) is active in all phases of passenger car category development, and the Society of Automotive Engineers (SAE) is the technical society for those with interest in transportation. Within the SAE is a Fuels and Lubricants

Division/Engine Oil Technical Committee (TC-1), which serves as a forum for open discussion of technical issues related to current and future engine lubrication needs and standards development. With the introduction of GF-3, the industry will move to a completely new set of engine tests for validation of passenger car engine oil performance. Although some new tests replace current tests, which are running out of parts, other provide a means to measure performance in new areas.

Among the GF-3 test, the most critical engine tests related to antiwear/EP performance are the Sequence IVA and the Sequence IIIF. The Sequence IVA is an ASTM designation of a test previously referred to as the KA24E, originally developed by the Japan Automotive Manufacturers Association. It is included to replace the wear component of the Sequence VE. The Sequence IVA is designed to evaluate an oil's ability to prevent cam lobe wear in slider valve train design engines operated at low-temperature, short-trip, "stop-and-go" conditions (low-speed/low-temperature operation). The test conditions and specifications are listed below:

Engine:	Nissan 2.4 L inline 4 cylinder
Engine speed:	800 and 1500 rpm cycles
Engine torque:	25 Newton-m
Oil temperature:	50–60°C
Cycle duration:	50min—low speed/10 min—high speed
Test length:	100 hr
7-Point cam lobe wear	120 μm max

The Sequence IIIF is a replacement for the Sequence HIE and uses a current production version of the GM 3800 Series II V-6 engine. Special camshaft and lifter metallurgy and surface finishing are used to increase wear. The sequence IIIF procedure is designed to evaluate an oil's resistance to oxidation and wear in high-speed and high-temperature vehicle operation. The test conditions and specifications are summarized below:

Engine:	GM 3800 Series II V-6 (231 CID)
Engine speed:	3600 rpm
Engine load:	200 Newton-m
Oil temperature:	155°C
Coolant temperature:	115°C
Test length:	80 hr
Average lobe and lifter wear	30 μm max

5 OUTLOOK

The additive industry has experienced a slight downturn in recent years. Despite the push for new engine oils meeting more stringent requirements, a major rationalization is occurring because of the ability to use additives longer and the recycling of products in the industry. Consequently, the total additive demand is growing very slowly (<2%). Ashless antiwear/EP additives are no different from other additives in terms of market demand.

Antiwear additives are a mature function class, and business opportunities in the next few year will be modest. The dominant position of zinc dithiophosphates in engine oils is not expected to be in jeopardy in the near term. Therefore, a total

switch to ashless antiwear additives in engine oils is not likely to occur soon, but minor changes are in progress.

The impetus for significantly improved lubricant additives is found on a number of fronts. Governmental and regulatory requirements continue to challenge the industry for improved products with lower toxicity. New engine developments, such as the ceramic diesel, are on the horizon, presenting opportunities for antiwear additives that can function at very high operating temperatures. Space technology and other advanced transportation needs present new challenges to the industry. And, of course, there will always be a need for low product costs and ease of production.

Four particular developments may have a major impact on the lubricant industry in the near term: (1) a move toward low-sulfur hydroprocessed (Groups II and III) and synthetic (Groups IV and V) base stocks; (2) the trend toward lower phosphorus in engine oils; (3) a desire to reduce or eliminate chlorine in lubricants, particularly in metal-working fluids; and (4) a move to eliminate heavy metals and/or achieve low ash or even ash-free from both engine oils and industrial oils.

To meet the growing needs for better thermal/oxidative stability and better viscometrics, synthetic base stocks such as polyalpha olefins, together with hydro-treated petroleum base stocks, are continuing to expand in all lubricant sectors. These types of materials have no aromatic hydrocarbons or greatly reduced amounts of aromatic hydrocarbons, which are potentially problematic. However, upon removing these solubilizing aromatics, the additives tend to precipitate out of the oil. This is particularly true for surface-active, polar components, such as antiwear additives. Therefore, greater compatibility with nonconventional base stocks (Groups II to V) will be an essential requirement for all ashless antiwear/EP additives. Meanwhile, there are noticeable synergies identified among certain ashless antiwear/EP additives and nonconventional base stocks in a number of lubricant applications. Therefore, the choice of proper ashless additives will be vitally important.

Because of the large number of automobiles equipped with catalytic converters that are sensitive to phosphorus derived from zinc dithiophosphates in the crankcase oil (possible reduction of catalytic efficiency), strong needs exist for engine oils with lower phosphorus content. This is expected to create a need for alternative antiwear/EP additives and antioxidant/anticorrosion additives, to partially replace zinc dithiophosphates, which possess all these functional properties.

Chlorine in lubricants and other materials is becoming an increasing environmental concern. Legislation around the industrial world limits the chlorine content of many lubricant products to 50 parts per million or less. The Montreal Protocol mandated a gradual phase-out of the use of chlorine-containing refrigerants, such as hydrochlorofluorocarbon (HCFC) and chlorofluorocarbon (CFC) and replacement with alternative hydrofluorocarbons (HFC). Increased wear occurred in the refrigeration compressor when HFC refrigerants were substituted for CFC, and the cause of this increased wear was believed to be inferior antiwear capability of the alternative HFC refrigerant as the environmental gas, compared to that for CFC [66]. This offers some opportunities for the development of new ashless antiwear additives for refrigeration compressor oils.

Similar ecological pressures are facing the cutting-oil industry, and future changes to reduce or eliminate chlorine are expected. The most significant opportunity is perhaps driven by human health and waste disposal issues concerning the use

of chlorinated paraffins. Chlorinated paraffins are used extensively as EP additives in metal-working fluids. The National Toxicology Program (NTP) listed chlorinated paraffins, derived from C12 feedstocks and chlorinated at 60%, as a suspect carcinogen. Although few metal-working fluids are formulated with this class of chlorinated paraffin, the image of chlorinated paraffins in general has suffered due to uncertainties about future NTP reclassification of all such additives.

Gear additives are another area of concern. Because of the problems associated with chlorine additives, their use in gear oils has been greatly reduced. However, a number of processes for making gear additives utilize chlorine or chlorine-containing reagents at some point in the reaction sequence. Small amounts of chlorine still remain in the final product. The complete removal of the chlorine is therefore expected to become an important priority, but will be difficult to attain in the near future.

Lastly, the use of metallic antiwear/EP additives is diminishing due to the influence of environmental concerns. Heavy metals are considered pollutants and their presence is no longer welcomed in the environment. Given equal performance and costs, ashless antiwear additives will be preferred for many future lubricants.

In the future, the lubricant additive business will continue to grow and will need more ashless antiwear/EP additives. Possible new markets include biodegradable lubricants, advanced transportation lubricants, robotics, ceramics, and space technology lubricants. Traditional markets in engine oils, automatic-transmission fluids, marine, aviation, gear, hydraulic, circulating oils, metal-working, and other industrial lubricants are also expanding. Healthy growth for nonconventional base oils (Groups II to V) is expected in many of these areas. Clearly, advanced ashless antiwear additives with environmentally friendly features, excellent stability, and unique performance properties, especially for nonconventional base oils, will be the additives of choice for increasingly demanding lubricant applications.

Acknowledgment

I would like to thank Pat Lorenz and Charles Cianci for assistance in the literature search and many of my colleagues, especially Dr. Andy Horodysky and Dr. Andy Jackson, for their valuable comments.

References

1. MW Ranney. Lubricant additives. *Chemical Technology Review*, no. 2, 1973.
2. MW Ranney. *Synthetic Oils and Additives for Lubricants—Advances Since 1977*. Noyes Data Corp., Park Ridge, NJ, 1978.
3. MW Ranney. *Synthetic Oils and Additives for Lubricants—Advances Since 1979*. Noyes Data Corp., Park Ridge, NJ, 1978.
4. J March. *Advanced Organic Chemistry*, 2nd ed. Wiley, NY, 1977, p. 703.
5. JS Pozey et al. *Reactions of Sulfur with Organic Compounds*. Pergamon Press, NY, 1987; EE Reid. *Organic Chemistry of Bivalent Sulfur*. Chemical Publishing Co., NY, 1963; N. Kharasch. *Organic Sulfur Compounds*, vol. 1, 1961, Chs. 8, 10, and 20.
6. PS Landis. The chemistry of 1,2-dithiole-3-thiones. *Chemical Reviews* 65: 237, 1965.
7. SO Jones, EE Reid. The addition of sulfur, hydrogen sulfide and mercaptans to unsaturated hydrocarbons. *J Am Chem Soc* 60:2452, 1938.
8. RP Louthan. Preparation of mercaptans and thioether compounds. U.S. Patent 3,221,056 (1965); other related patents: U.S. Patents 3,419,614, 4,194,980, and 4,240,958.

9. U.S. Patents 2,012,446 and 3,953,347.
10. H. Myers. Lubricating compositions containing polysulfurized olefin. U.S. Patent 3,471,404 (1969); other related patents: U.S. Patents 3,703,504 and 3,703,505.
11. KE Davis. Sulfurized compositions. U.S. Patents 4,119,549 (1978) and 4,191,659 (1980); KE Davis, TF Holden. Sulfurized compositions. U.S. Patents 4,119,550 (1978) and 4,344,854 (1982); SA Dibiase. Hydrogen sulfide stabilized oil-soluble sulfurized organic compositions. U.S. Patent 4,690,767 (1987); AG Horodysky, DA Law. Additive for lubricants and hydrocarbon fuels comprising reaction products of olefins, sulfur, hydrogen sulfide and nitrogen containing polymeric compounds. U.S. Patent 4,661,274 (1987).
12. AG Horodysky. DA Law. Sulfurized olefins as antiwear additives and compositions thereof. U.S. Patent 4,654,156 (1987); related patent: U.S. Patent 2,995,569.
13. DE Johnson et al. Sulfurized olefin extreme pressure/antiwear additives and compositions thereof. U.S. Patent 5,135,670 (1992); other related patents: U.S. Patents 2,999,813, 2,947,695, and 2,394,536.
14. AG Papay. Lubrication Engineering 32(5): 229–234, 1975.
15. PS Korosec et al. NLGI Spokesman 47 (1), 1983.
16. I Macpherson et al. NLGI Spokesman 60 (1), 1996.
17. O Rohr. NLGI Spokesman 58 (5), 1994.
18. AG Papay. Lubrication Science 10-3, 1998.
19. RM Mortier, ST Orszulik. Chemistry & Technology of Lubricants, Blackie, London and VCH Publishers, Inc., New York, New York, 1992.
20. D Samuel, BL Silver. J Chem Soc. 675(3):3582, 1963.
21. TD Smith. J Chem Soc. 210(1):1122. 1962.
22. DL Venezky et al. J Am Chem Soc 78: 1664, 1956.
23. HD Orloff. J Am Chem Soc 80: 727–734, 1958.
24. IN Lacey, PB Macpherson, HA Spikes. Thick antiwear films in EHD contacts, part 2: Chemical nature of the deposited film. ASLE Preprint, 1985.
25. DEC Corbridge. Phosphorus: An Outline of Its Chemistry, Biochemistry, and Technology, Elsevier Science BV The Netherlands, 1985, pp 213, 249, and 401.
26. RM Lange. Norbornyl dimer ester and polyester additives for lubricants and fuels. U.S. Patent 4,707,301 (1987).
27. K Pollak. Amine derivative of dithiophosphoric acid compounds. U.S. Patent 3,637,499 (1972).
28. H Shaub. Amine salt of dialkyldithiophosphate. U.S. Patent 4,101,427 (1978).
29. KP Michaelis, HO Wirth. Di-or trithiophosphoric acid diesters. U.S. Patent 4,244,827 (1981).
30. AG Horodysky, RM Gemmill. Phosphosulfurized hydrocarbyl oxazoline compounds. U.S. Patent 4,255, 271 (1981).
31. LO Farnig et al. Phosphorodithioate-derived pyrrolidinone adducts as multifunctional antiwear/antioxidant additives. U.S. Patent 5,437,694 (1995).
32. DE Ripple. Phosphorus acid compounds—acrolein-ketone reaction products, U.S. Patent 4,081,387 (1978).
33. LO Farnig et al. Lubricant additive comprising mixed hydroxyester or diol/phosphorodithioate-derived borates. U.S. Patent 4,784,780 (1988).
34. AB Cardis. Reaction products of dialkyl and trialkyl phosphites with elemental sulfur, organic compositions containing same, and their use in lubricant compositions. U.S. Patent 4,717,491 (1988).
35. DS Bosniack. U.S. Patent 4,079,012 (1978).
36. JW Nebzydoski et al., U.S. Patent 3,952,059 (1976).
37. H Debus. Über die Verbindungen der Sulfocarbaminsäure. Ann. Chem. (Liebig's) 73:26, 1850.

38. GD Thorn, RA Ludwig. *The Dithiocarbamates and Related Compounds*. Elsevier Pub, Amsterdam (1962).
39. WY Lam. U.S. Patent 4,836,942 (1989).
40. AB Cardis et al. Borated dihydrocarbyl dithiocarbamate lubricant additives and composition thereof. U.S. Patent 5,370,806 (1994).
41. LO Farnig et al. Dithiocarbamate-derived ethers as multifunctional additives. U.S. Patent 5,514,189 (1995).
42. RQ Little. U.S. Patent 3,087,932 (1963).
43. RM Gemmill et al. U.S. Patent 4,584,114 (1986).
44. RH Davis et al. Antiwear/antioxidant additives based on dimercaptothiadiazole derivatives of acrylates and methacrylates polymers and amine reaction products thereof. U.S. Patent 5,188,746 (1993).
45. TJ Karol. Maleic derivatives of 2,5-dimercapto-1,3,4-thiadiazoles and lubricating compositions containing same. U.S. Patent 5,055,584 (1991).
46. EK Fields. U.S. Patent 2,799,652 (1957).
47. RH Davis et al. Dimercaptothiadiazole-derived, organic esters, amides and amine salts as multifunctional antioxidant/antiwear additives. U.S. Patent 4,908,144 (1990).
48. PW Vogel. U.S. Patent 3,759,830 (1973).
49. EK Fields et al. U.S. Patents 2,703,784 and 2,703,785 (1955).
50. S-Y Hsu et al. Quaternary ammonium salt derived thiadiazoles as multifunctional antioxidant and antiwear additives. U.S. Patents 5,217,502 and 5,194,167 (1993).
51. J Zhang et al. A study of 2-alkyldithio-benzoxazoles as novel additives. *Tribology Letters* 7: 173–177, 1999.
52. AT Polishuk, HH Farmer. *NLGI Spokesman* 43:200, 1979.
53. R Schmacher et al. Improvement of lubrication breakdown behavior of isogeometrical phosphorus compounds by antioxidants. *Wear* 146: 25–5, 1991, and *Tribofragmentation and antiwear behavior of isogeometric phosphorus compounds*. *Tribology Intl* 30 (3) 199, 1997.
54. AOM Okorodudu. Organophosphorus derivatives of benzotriazole. U.S. Patent 3,986,967 (1976).
55. LO Farnig, AG Horodysky. Phenylenediamine-derived phosphonates as multifunctional additives for lubricants. U.S. Patent 5,171,465 (1992).
56. BW Hotten. Bisphosphoramides. U.S. Patent 3,968,157 (1976).
57. DL Andrew, GG Moore. Lubricating grease composition with increased corrosion inhibition. EP-903398, 1999.
58. RJ Cier, RF Bridger. U.S. Patent 4,025,446 (1977).
59. RJ Pratt. U.S. Patent 3,941,808 (1976).
60. NL Avery et al. Friction modifiers and antiwear additives for fuels and lubricants. U.S. Patent 5,538,653 (1996).
61. LO Farnig et al. Triazole-maleate adducts as metal passivators and antiwear additives. U.S. Patent 5,578,556 (1996).
62. LO Farnig et al. Fuel composition comprising triazole-derived acid-esters or ester-amide-mine salts as antiwear additives. U.S. Patent 5,516,341 (1996).
63. *Lubrication Engineering* 35(5):266–271, 1979.
64. MJ Furey, C Kajdas. Wear reducing compositions and methods for their use. U.S. Patent 5,880,072 (1999).
65. JR Baranski, CA Migdal. Phenolic borates and lubricants containing same. U.S. Patent 5,698,499 (1997).
66. K Mizuhara et al. The friction and wear behavior in controlled alternative refrigerant atmosphere. *Tribology Trans* 37(1): 120, 1994.

Sulfur Carriers

THOMAS ROSSRUCKER and ACHIM FESSENBECKER

Rhein Chemie Rheinau GmbH, Mannheim. Germany

1 INTRODUCTION

In the lubricant industry a great variety of sulfur-containing additives are known and in use today. We list only a few of the most common types:

- Sulfur carriers (sulfurized olefins, esters, and fatty oils)
- Sulfur/phosphorus derivatives (dithiophosphates, thiophosphonates, thiophosphites, etc.)
- Thiocarboxylic acid derivatives (dithiocarbamates, xanthogenates, etc.)
- Heterocyclic sulfur (mercaptobenzothiazoles, thiadiazoles, etc.)
- Sulfonate (Na, Ca salts of alkylbenzenesulfonic acids, nonylnaphthalenesulfonates, etc.)
- Others (sulfated fatty oils/Turkish red oils, sulfurchlorinated fatty oils, sulfur-linked phenols and phenates)

This long list gives a good impression of the versatility and importance of sulfur chemistry in lubricants. But as versatile as their chemistry is, as versatile is the range of application of sulfur-containing lubricant additives. In this chapter we try to review major aspects of a group of additives commonly known as “sulfur carriers.” This is a generic name that has been accepted in the marketplace and used to summarize a group of additives that provide extreme-pressure (EP) and antiwear (AW) properties and are used in gear oils, metal-working fluids, greases, and engine oils. The vast majority of them are sulfurized fats, esters, and olefins. In order to distinguish them from other sulfur-containing products and avoid misunderstandings, a suitable definition for sulfur carriers is the following: Sulfur carriers are a class of organic compounds

that contain sulfur in its oxidation state, 0 or -1
where the sulfur atom is bound either to a hydrocarbon or to another sulfur
atom
that do not contain other hetero atoms except oxygen
produced by adding sulfur to all kinds of unsaturated, double-bond-containing
compounds such as olefins, natural esters, acrylates, and others

Lubricant additives fitting this definition are the main focus of this chapter. Due to the overwhelming versatility of sulfur chemistry, other sulfur-containing product groups cannot be discussed in depth but are mentioned in the context where appropriate.

Despite the fact that this group of additives has been used in the lubricant industry for more than seven decades, sulfur carriers are not at all an endangered species. In fact, we are still seeing increasing usage today. This is partly due to continuously ongoing R&D work done in this area that brings about innovation and product improvement. Also, many chemical aspects and applications are waiting to be discovered. Furthermore, sulfur carriers are essential additives for the solution of upcoming lubricant market requirements such as “chloroparaffin substitution,” “heavy-metal replacement,” and “health and safety issues.” Therefore, we expect to see substantial future growth of light-colored and low-odor sulfur carriers.

2 HISTORY

As we looked back on more than 100 years of sulfurized compounds, we had to rely on literature sources for the time before the 1950s. During the literature studies it turned out that one of the most fruitful sources for the time period before 1950 is the review articles of Helen Sellei [1,2] published in 1949. Much of what follows is based on their content, but we have tried to reinterpret the information with today's background knowledge.

2.1 First Synthesis and Application (1890–1918)

Sulfurized fatty oils have been commercially produced for more than 100 years. Long before they were used as additives in lubricants, they had become important additives for the rubber industry. The addition of 4–8% sulfur to an unsaturated natural oil such as rape seed oil at high temperatures (120–180°C) gives a flexible, gummy polymer called “factis.” The sulfur undergoes an addition reaction to the double bonds of the natural oil and builds up a three-dimensional structure of sulfur bridges between the triglyceride molecules.

In the late 19th century, rubber was an expensive natural raw material and with the rapid industrialization in general and the growing automobile industry in particular, rubber tires were needed in increasing amounts. It soon turned out that factis also provided special, positive properties to rubber goods during the vulcanization process. This was the starting point of smaller chemical factories producing additives for the rubber industry. In 1889 Mr. Benz submitted the patent for the world's first automobile in Mannheim, Germany. In the same year and city, Rhein Chemie Rheinau GmbH was founded and started to produce sulfurized natural oils. Germany had seen a special national aspect to the industrial history of sulfurized fats and rubber before 1914. Because Germany had very few colonies, all rubber had to be

imported. During the international tensions in the first decade of the 20th century and subsequent trade boycotts, the search for alternatives had been strongly pushed, leading to the development of synthetic rubber ("Buna"). Subsequently, because it was cheap and based on locally available raw materials, factis had found increasing use as a rubber substitute and rubber diluent.

2.2 First Application in Metal-Working Oils (1920–1930)

In the very early days of modern lubrication it had become known that sulfur is an important element to improve frictional properties and to prevent seizure under high loads. Free sulfur as well as sulfur-containing heterocyclic molecules are known as part of natural crude oil (thiophenes, thioethers, etc.). In early refining technology they were not removed effectively, especially from the higher-viscosity oils that were typically used for gear oils that had up to 3–4% sulfur. This natural sulfur contributed to mild EP performance (antiwelding). After the positive effects of sulfur for lubricant oil formulations were recognized, the next step was to physically dissolve sulfur flower at elevated temperatures into the lubricant oil. This sulfur, however, is very reactive and corrosive against copper and its alloys. Also, sulfur flower has a limited solubility in mineral oil, which limits its maximum dosage and the final EP performance achievable.

Sulfurized esters were first used in metal working. For heavy-duty operations with a high degree of boundary lubrication, it was realized that the addition of oil-soluble sulfur compounds had a tremendous effect on the performance. The first milestone literature that reports this effect was published in 1918 by the E.F. Houghton Corporation [3] for cutting oils. It is claimed that a mixture of lard oil, mineral oil, and wool fat treated with sulfur flowers at elevated temperatures results in a sulfurized product that increases the performance of cutting oils enormously. In particular, the tool life is extended and smoking of the coolant is reduced greatly due to friction and temperature reduction. These observations are still valid today and may be considered the starting point of the application of sulfur carriers as additives for lubricants.

In comparison to the solid, rubberlike material factis, which has been commercialized for several decades, Houghton Corp.'s breakthrough was to produce a liquid fatty material that was soluble in mineral base oil at any ratio. It overcomes the solubility limits of sulfur flowers and allows the adjustment of the EP performance level according to treat rate. They achieved this simply by using nonreactive mineral oil and wool wax as chain-breaking agents and diluent to control the polymerization reaction of lard oil to keep it liquid. From thereon, the use of sulfurized oils became quite common in metal working.

2.3 Sulfurized Compounds for Gear Oils and Other Lubricants (1930–1945)

Some years later, the idea of improving load-carrying capacity under high-pressure, high-temperature conditions had been picked up by automotive lubricant researchers and applied to the newly constructed hypoid gear oils. With the advent of hypoid gears in automotive applications in the 1920s and 1930s, wear and seizure under high-load conditions became a major technical problem that lubricant oil companies needed to solve. Most of the development work had been done within these lubricant

companies, and the new technology had not been published in detail. However, the number of patents on sulfur compounds for lubricants developed very rapidly throughout the 1930s and 1940s:

- 1936 First patent review on EP lubricants [4]
- 1940 Patent review 1938–39 [5]
- 1941 General publication on lubricating additives including an extensive patent bibliography [6]
- 1946 Review article on sulfurization of unsaturated compounds [7]

This clearly indicates that the ideas invented and first applied by the metal-working people also worked for gears. Combinations of sulfurized products with lead soaps and lubricity esters were the first high-EP performance technology in gear oils. Many years later Musgrave stated in an article on hypoid gear oils [8] that it was just by chance that the synergistic effect of sulfur with lead soaps had been discovered in the early 1930s.

An interesting historical dimension was added to the EP-gear oil development during World War II. Most of the gear oil development occurred in the United States due to the great importance of the automobile industry in the 1920s and 1930s. German gear oil technology was not as advanced. Eyewitnesses report frequent gearbox failures of German tanks and heavy equipment during the attack on Russia. The reason was that in autumn Russian roads were turning into mud and the heavy vehicles were operated most of the time at maximum performance. The only mildly additized gear oils just were not good enough to prevent scoring and welding.

2.4 Scientific Research on Chemistry and Application (1930–1949)

Between 1930 and 1950 the important basics of sulfurized carrier technology had been developed. Patents from this period include most of today's raw materials and reaction pathways. Raw materials were animal oils [9], vegetable oils/organic acids [10], pine oils [11,12], whale oil (sperm oil), acrylates, olefins [13], alcohols [14], synthetic esters [15], and salicylates [16]. Even thiocarbonates [17] and xanthogenates [18] were synthesized and used as organic, oil-soluble sulfur-based EP additives. Reaction pathways mentioned in these patents include

- Sulfur flower reaction with and without H_2S , aminic, and other suitable catalysts
- sulfurchlorination with S_2Cl_2 [19]
- organic halides with alkalipolysulfides
- mercaptan route [20]

- Important product properties that are still part of today's development work were also mentioned also in that period:
 - stability of sulfurized products, e.g., diisobutene [21]
 - active and inactive sulfur compounds
 - corrosive and noncorrosive compounds
 - light- and dark-colored derivatives
 - high- and low-odor products

Parallel to new chemistry, the development of test machines for tribological research progressed quickly along with publications on mechanistic studies

of additives. In 1931 at an API meeting Mougay and Almen [22] presented the first chemical interpretation for the load-carrying capacity of sulfur-containing EP additives and their synergy with lead soaps. They attributed the performance to the formation of a separating film between the factional partners—a theory generally accepted and proven today. In 1939 this film-forming theory of sulfur compounds was proven using the four-ball tester [23]. In 1938 Schallbock et al. published [24] standard-setting results on investigations in the field of metal working. Empirical correlations were found between cutting speed, temperature, and tool life that are still valid. In 1946 synergistic effects of chlorinated additives with sulfur additives were explained based on a chemical reaction theory [25] under the aspect of newest-generation hypoid gear formulations. Phosphorus additives [tricresylphosphate [26], zinc dialkyldithiophosphates (ZnDTP)], primary antioxidants (phenyl- α -naphthylamine, butylated hydroxytoluene, BHT), detergents/dispersants [27] (salicylates) also joined the world of additives in this period and have been used since in combination with sulfur carriers.

Most of the development work at that time had been done in a deductive way in a trial-and-error approach. Theoretical explanations and tribological and chemical modeling always trailed behind (looking back from today's point of view, it is quite astonishing that not so much has changed in 70 years).

2.5 Summary of the Last 50 Years

With the fundamentals of sulfur carriers being explored so early in lubricant oil additive history, the literature from 1950 until today concentrates around improvements in production procedures, combinations and synergies with other additives, improvement in product qualities, and search for special applications. The use of sulfur carriers has been extended from metal working and automotive to industrial oils and greases. Ashless hydraulic oils may contain sulfurized EP additives for special applications. Now this product group is used throughout the lubricant oil industry.

“Tribology” has been defined as a particular field of scientific research, and several basic models of additive response have been worked out properly. A review article [28] in 1970 summarizes the state of the art at that time, including many literature references.

Until the 1950s the sulfur carriers were mostly made by the lubricant oil manufacturers. However, increasing environmental awareness, growing markets, and the need for more specialized products brought about change. As the sulfurization process involves deep chemical knowledge and production know-how and includes extremely high safety risks, this field has been taken over by chemical companies. It is expected that the few, smaller lubricant oil companies that still produce a small quantity of black sulfurized fats in-house will cease production sooner or later.

In the 1950s the sulfur carrier market was split into two segments: automotive and industrial. The large oil companies already had their chemical departments (Mobil Chemical, BP Chemical, Shell Chemical, Exxon Chemical, etc.). They opened additive units as the market grew. They had and still have their main market in automotive applications. In automotive gear oils sulfurized isobutene soon

became the standard product because it is high in sulfur content but low in corrosivity. The typical, rather strong smell is not a big issue because gearboxes are totally closed systems. So the major companies went into large-scale production of sulfurized isobutene. Over the decades these products have gone through changes in chlorine level due to environmental requirements [29]. Starting at 2–3% in the early days, today high-quality products no longer contain chlorine because of a chlorine-free, high-pressure H_2S production process. Also, the amount of active sulfur in sulfurized isobutene has been reduced to improve the long-term abrasive wear of gear oil formulations in bearings and to meet today's "fill-for-life" requirements. But in principle in automotive applications the same sulfur chemistry is in use today as it was 60 years ago.

The industrial market requires much more problem-solving additives, and a variety of smaller-volume sulfur carriers is needed to address different grease and metal-working applications and satisfy speciality requirements. Subsequently specialized chemical companies started with the production of sulfur carriers for industrial oils. Having a long-term background in sulfurization of fatty oils for rubber applications, our company started to market specialized sulfur carriers for industrial applications in 1957. The first products were dark in color, but as early as 1962 Rhein Chemie commercialized its first light-colored and low-odor sulfurized synthetic ester based on chlorine-free production technology (see below).

A big milestone in the history of sulfur carriers has been the international banning of sperm oil (whale oil) in 1971, which was commonly used as high-quality and cheap raw material. The sulfurized products based on this raw material showed excellent solubility and lubricity. The extensive research activities of this period resulted in a variety of patents [30,31]. The new raw materials turned out to be vegetable oils in combination with either synthetic esters or olefins.

Another aspect that strongly influenced the sulfur carrier market has been the change of refinery technology for base oils. The aromatics and the sulfur content have been reduced more and more. Regarding the first point, the effect on the additives including the sulfur carriers has been that they needed adjustment of their solubility properties in order to avoid turbidity problems in the less polar base fluids. The second point, of course, has contributed to a growing market of sulfurized additives because the natural sulfur, which also contributes to EP/AW as well as antioxidant performance, needed to be balanced with additives. This trend started in the 1970s but is getting stronger today with the XHVI base oils/Groups II and III as well as fully synthetic base stocks (polyalphaolefins).

Another market requirement that contributed to an increasing sulfur carrier production in the 1980s has been from lubricant oil producers. Many companies just did not like to sulfurize their base oils for metal-working applications or running in gear oils any longer and were asking for solutions. The solution offered from the additive manufacturers has been the organic polysulfides of light color and rather low odor. Diisobutenepentasulphide and tertiary dodecylpentasulfide have been introduced as easy-to-blend, liquid substitutes for sulfur flower. This happened around the end of the 1970s to the early 1980s. Today these active-type pentasulfides have become the most important and widespread subgroup of sulfur carriers on the industrial oil side.

In 1985 it was found that sulfur carriers, preferably polysulfide types, show a strong synergistic EP/AW behavior when combined with high total base numbers (TBN), sodium and calcium sulfonates [32]—similar to what was found in the 1930s with chlorinated paraffins. This has become known as the “PEP technology” (passive extreme pressure) in neat oil metal working. In the beginning, it was hoped that this combination would be a general and simple solution to the upcoming chlorine paraffin replacement issue that started in Middle Europe and Scandinavia in the mid- to late-1980s. Unfortunately, this is not the case. Combinations of chlorine/sulfur cannot just simply be substituted by combinations of overbased products/sulfur technology due to the universal all-around properties of chlorinated paraffins—a fact that made the chlorinated paraffins the backbone of many metal-working oils up to that time (*for more details see Section 5.4.2, Basic Alkali Metal Salts*).

In the late 1980s to the early 1990s, a totally new aspect of sulfurized fats gained substantial ground—the toxicology and ecotoxicology of these chemicals. Workers’ safety, environmental compatibility, biodegradability, and similar requirements needed to be addressed in industrial more than in automotive lubrication. The fact that the use of natural, renewable raw materials and optimized production procedures may give low toxic and biodegradable sulfur carriers refreshed the interest of development chemists in these special, environmentally safe but classic additives.

3 CHEMISTRY

3.1 Chemical Structure of Sulfur Carriers

For the majority of sulfur carriers discrete structures are very hard to sketch for several reasons:

The raw materials are very often mixtures of isomers: in the case of olefins, for example, diisobutene, there are five main isomers; tetrapropylene shows more than 50 components in the gas chromatogram (GC). Natural fatty oils have a distribution with mono-, double-, and triple unsaturated acids plus unsaponifiable matter.

Depending on the temperature, inter- or intramolecular bonding of sulfur occurs preferably.

The catalyst directs the addition of sulfur in a certain way (“Markovnikov,” etc.).

It is a fact that sulfur carriers are technical products based on technical raw materials. In the following, the most typical structures of sulfur carriers based on different, contemporary raw materials are shown. Taking the rather complex reaction pathways of a sulfurization reaction into account, they necessarily are simplified model structures.

3.1.1 Sulfurized Isobutene

This is the standard EP additive for gear oils with typical sulfur contents in the range of 40–50%.

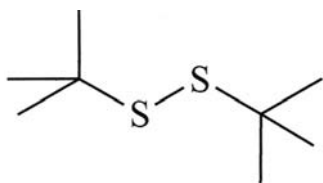


Figure 1 Sulfurized isobutene.

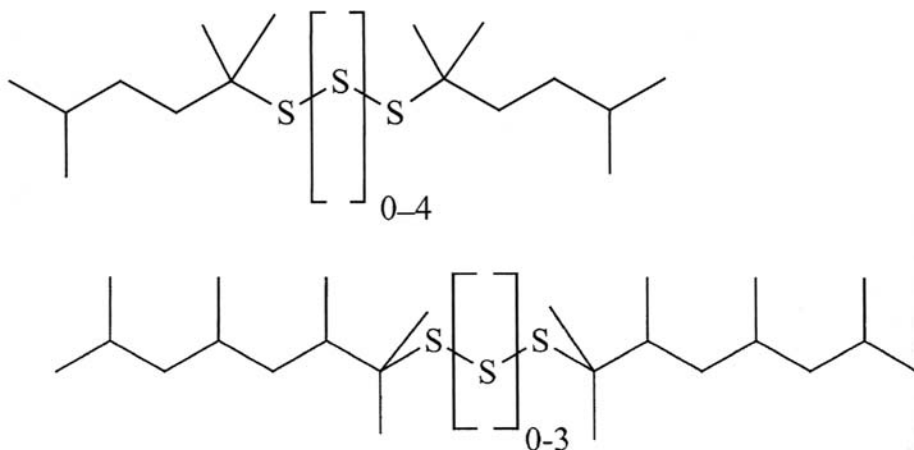


Figure 2 Sulfurized diisobutene, sulfurized tetrapropylene.

3.1.2 Active-Type Sulfurized Olefins

These are the polysulfide types of sulfur carriers that have been introduced as a substitute for sulfurization of base oil and are widely used today in metal-working applications (Figure 2).

3.1.3 Inactive Sulfurized α -Olefins

These are used in noncorrosive lubricant applications ranging from metal working, greases, and even engine oil applications (Figure 3).

3.1.4 Sulfurized Synthetic Esters (Light Color)

These are widely used in metal-working and grease applications. Depending on the type of synthetic ester chosen, special properties such as low-temperature stability/fluidity and low viscosity may be achieved (Figure 4).

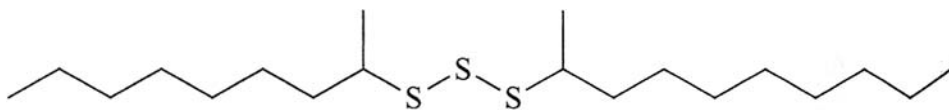


Figure 3 Inactive sulfurized α -olefins.

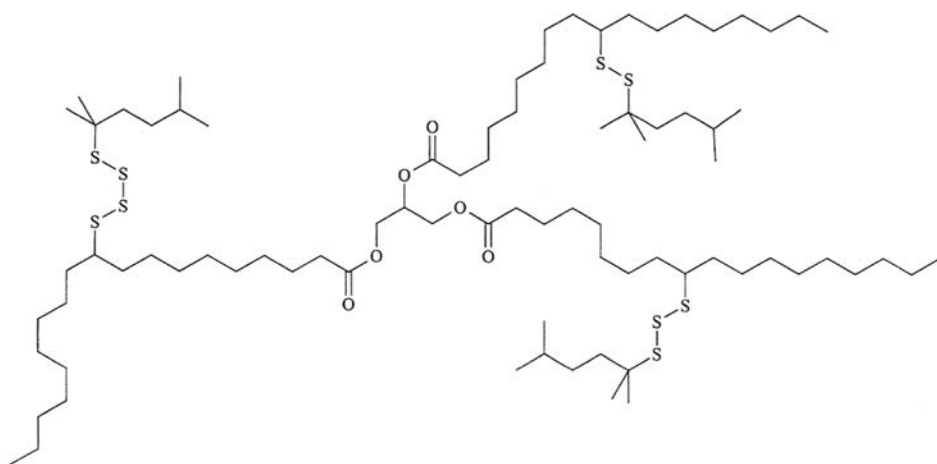


Figure 6 Sulfurized fatty oil/olefin mixture (light color).

double bonds, and textbook chemistry applies to this kind of reaction (catalytical conditions, mechanisms, addition patterns— “Markovnikov, anti-Markovnikov orientation”).

Today’s large-scale production technology in general avoids any halogen-containing reaction steps because there are low limits (max. 30 ppm chlorine) in the final lubricants that may not be exceeded, e.g., in automotive gear oils. Also, expensive removal/work up steps, e.g., by washing, etc. can be avoided if halogens are not used.

Any sulfurization process involves either the possible formation or the actual use of hydrogen sulfide (H_2S), an extremely toxic and corrosive gas. The smell of H_2S is generally known as the smell of rotten eggs, which is offensive to the human nose. In earlier times, the H_2S released during the sulfurization reaction (*see Section 3.2.2, Black Sulfurization*) was just vented through a chimney or, if at all, scarcely absorbed in alkaline scrubbers. Today this procedure is no longer tolerated almost worldwide, and smaller factories that have not yet done so need to invest into expensive safety equipment. This is another reason why the smaller lubricant oil companies that still do a little sulfurization are considering stopping. The processes are either pure batch or semicontinuous. For industrial applications the volumes and varieties would not justify fully continuous productions.

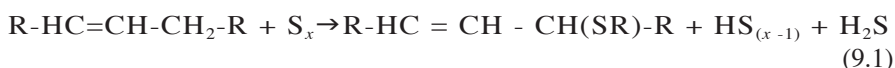
3.2.2 Black Sulfurization

This is the simplest and oldest of all production technologies for sulfur carriers. The first patented sulfur carrier was done this way. The manufacturing equipment needs to withstand pressure up to 1–2 bar (it may even be pressurized less). Raw materials may be olefins as well as natural or synthetic esters with a certain degree of unsaturation. The other reactant introduced into the olefin-containing reaction vessel is sulfur flowers. The mixture is heated above the melting point of sulfur. An uncatalyzed reaction starts to become exothermic above 150–160°C, with the evolution of

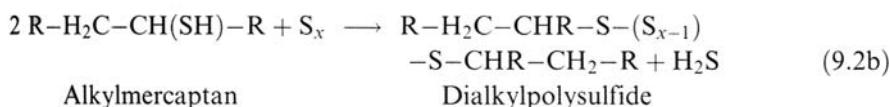
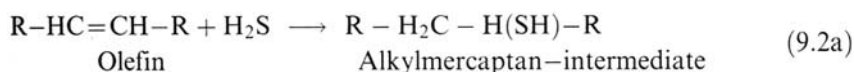
substantial amounts of H_2S . Catalyzed reactions start already just above the melting point of sulfur, in the range of 120–125°C. Typical catalysts are organic amines, metal oxides, and acids.

Mechanistic studies of this reaction have been reported [33] and are very complex. At temperatures between 120–160°C, intermolecular reactions are preferred. At 160–190°C, intramolecular reactions may be detected.

The first reaction step in this so-called black sulfurization process is the ring opening of the sulfur flower (S_8 ring structure) and the subsequent oxidative attack of the sulfur on the vinylic protons [Eq. (1)]. This quite uncontrolled reaction ends in the release of H_2S and the formation of vinylic mercaptans, vinylic thioethers, vinylic alkyl- and dialkylpolysulfanes, vinylic thioketones, and even sulfur-containing heterocycles (thiophenes, etc.).



A great part of the in situ generated H_2S does not leave the reaction mixture but is directly adsorbed by the double bonds, thus producing saturated alkylmercaptans [Eq. (2a)]. They react further oxidatively with sulfur flowers to generate alkyl- and dialkylsulfides with the release of more H_2S (2b):



The final product consists of a full range of organic sulfur derivatives. Some of them are still unsaturated, with isomerized double bonds and conjugated, chromophoric (color-deepening) sulfur compounds such as thioketones and thiophenes, which cause the product to be dark black in color and rather smelly. From an application point of view these products exhibit EP/AW performance, but because of their remaining double bonds have the following negative characteristics:

1. They will continue to polymerize during use and even under normal storage conditions.
2. They are easily oxidizable and form residues on fresh metal surfaces and discoloration.
3. They will cause TAN increase within a short time in circulation systems and cause short oil drain intervals.
4. They will even generate H_2S /mercaptan during high-temperature usage in lubricant systems.

(See the *Stability, Polymerization subsections of Section 4.2.1*.) So today's main use of these black sulfurized products are total loss lubricants where long-term stability and bad smell are not an issue. It is the cheapest way of making sulfurized additives.

3.2.3 High-Pressure H₂S Reaction

High-quality sulfur carriers, which have improved properties compared to the black materials, are produced today using high-pressure, high-temperature equipment. The handling of toxic H₂S under high-pressure conditions requires sophisticated handling techniques and safety measures. Furthermore, H₂S is an extremely expensive gas. All these aspects contribute to significantly higher production costs compared to the simple black sulfurization.

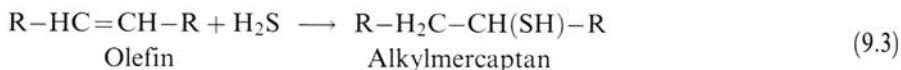
In this process, the olefins, sulfur, and H₂S are added to a high-pressure reactor and heated to 120–170°C. The reaction is also catalyzed by amines, metal oxides, acids, etc. For low-boiling olefins such as isobutene the pressure may go up as high as 50–60 bar. For higher-boiling olefins such as diisobutene typical pressures are in the range of 2–15 bar. The presence of H₂S as a reducing agent and strong nucleophile makes a total difference to the black sulfurization process. The oxidative attack of sulfur on the vinylic carbon-hydrogen (C–H) bond is effectively suppressed. The side reaction of the black sulfurization process becomes the main reaction here: the addition of H₂S to the double bonds to form mercaptans [Eq. (2a)], which then quickly react with sulfur in a redox reaction to form dialkyldi-, tri-, tetra-, and polysulfides plus release of one mole equivalent of H₂S (2b).

This procedure gives much more controlled reaction conditions and finally fewer side products. The most important effect of this reaction pathway is the fact that the double bonds are gone after the reaction and that no conjugated systems with chromophore (color-deepening) properties of H₂S can be formed. The sulfur carriers produced this way are much more oxidatively stable and they are of light color. This one-step-process is an advantage in terms of total production time and turnover.

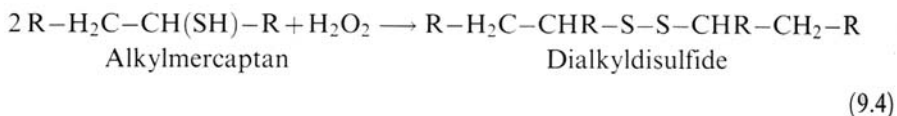
3.2.4 Mercaptan Route

Few producers synthesize sulfur carriers in a two-step process.

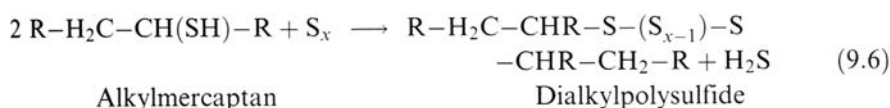
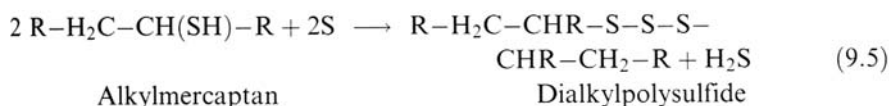
1. In the first step hydrogen sulfide is added to olefins under the catalytic action of Lewis acids. If such strong activators as BF₃ are used, the reaction takes place as low as -20°C. Another procedure works at 60–90°C. The resulting alkylmercaptans are distilled from the reaction mixture and isolated as intermediates [Eq. (3)]. The nonreacted olefins are circulated back to the reaction vessel.



2. The mercaptans are oxidized with either H₂O₂ [hydrogen peroxide, Eq. (4)] to the dialkyldisulfides:



or by stoichiometric amounts of sulfur to trisulfides [Eq. (5)] and polysulfides [Eq. (6)]:



This may be summarized in the equation shown in Figure 7.

This process is mainly applied to olefin-based sulfur carriers based on tri- and tetrapropylene as starting material because the resulting tertiary dodecylmercaptan may be used in other applications such as rubber processing and as a chemical intermediate.

3.3 Other Synthetic Routes

3.3.1 Sulfurchlorination and Dechlorination

Originally this has been a very widely used reaction pathway to make sulfurchlorinated fatty oils, where the product of reaction (7) is already the desired material—and sulfurized isobutene, where a second reaction step is followed (8).

Disulfurdichloride is the sulfur-containing raw material for this process. It is a very controlled way of adding discrete S_2 -bridges to double bonds with few side reactions occurring. At the same time chlorine is introduced into the molecule, giving additional EP performance. The sulfurchlorinated fatty oils are still used in some heavy-duty metal-working processes. From a technical point of view their biggest problem is the split-off of chlorine and subsequent severe corrosion problems, which are difficult to control. From today's point of view, the presence of chlorine is not favorable because of environmental problems.

In order to get low-chlorine-containing compounds, the reaction product of Eq. (8) is further treated with Na_2S in a second reaction step. It is a substitution

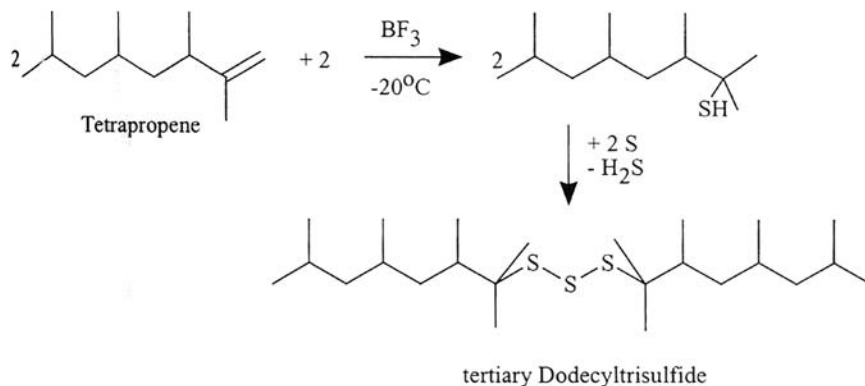


Figure 7 Summary of two-step process.

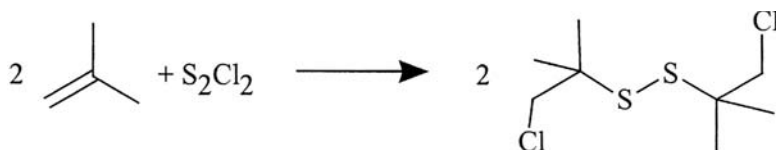


Figure 8 Sulfurchlorinated fatty oils.

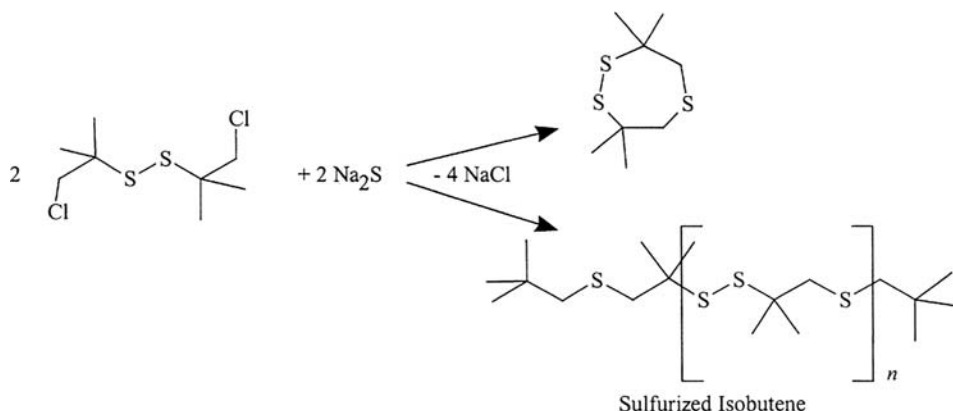


Figure 9 Sulfurized isobutene.

reaction of sulfur versus chlorine (9). Intermolecular linkage as well as ring closure may occur. The inorganic sodium chloride is washed out with water.

3.3.2 Alkylhalogenide /NaS_x

This process is closely related to reaction (8). Starting materials may be alkyl- or arylhalogenides. As in Eq. (9), it is possible to substitute halogens with sulfur using alkali sulfides. If Na₂S is used, monosulfides are generated. In case alkali polysulfide is applied, alkyl- or arylpolysulfides are the resulting derivatives.

This route has not found commercial interest as raw material costs are too high compared to other synthetic methods.

3.4 Raw Materials

In principle any single- or multi-double-bond-containing molecule may be sulfurized. Therefore, the list of olefinic raw materials is long. The list of sulfur-containing materials is rather short. It is mainly sulfur flowers (S₈), hydrogen sulfide gas (H₂S), little S₂Cl₂, and little alkali polysulfide (e.g., NaS_x).

On the olefin side, patent literature reports the following:

Vegetable oils (soy bean, canola, rape seed, cotton seed, rice peel, sunflower, palm, tall oil, terpenes, etc.)

Animal fats and oils (fish oils, lard oil, tallow oil, sperm oil, etc.)

Fatty acids

Synthetic esters

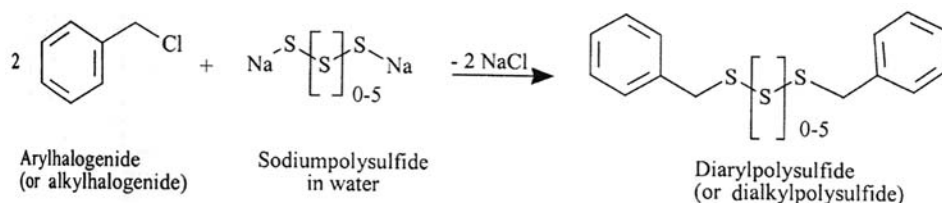


Figure 10 Alkyl- or arylpolysulfides result when alkali polysulfides is applied.

Olefins (isobutene, diisobutene, triisobutene, tripropylene, tetrapropylene, α -olefins, n -olefins, cyclohexene, styrene, polyisobutene, etc.)
 Acrylates, methacrylates
 Succinic acid derivatives, and more

The choice of commercially applied raw material is certainly limited to those compounds that have a reasonable price level and give certain performance benefits. Sulfur carriers based on low-boiling olefins, (e.g., C₄ types) are limited to closed lubricating systems due to the volatility of the decomposition products associated with an offensive smell. For water-based lubricant oil systems, sulfurized fatty acids that can be easily emulsified and active types of olefins which cannot hydrolyze are preferred. In oil applications one can find the full range of products.

4 PROPERTIES AND PERFORMANCE CHARACTERISTICS

4.1 Chemical Properties

4.1.1 Effect of Additive Structure on Performance

Raw Materials

The additive structure is mainly influenced by the choice of the raw materials and the sulfurization method. A general overview of the performance properties of sulfurized products based on different raw materials is shown in Table 1.

Influence of Raw Materials on Extreme-Pressure and Antiwear

The raw material determines the polarity and, therefore, the affinity of the product to a metal surface [34]. With increasing polarity, an increasing extreme-pressure (EP)

Table 1 Performance Properties of Sulfurized Products

	Ester		Triglyceride		Olefins	
	Inactive	Active	Inactive	Active	Inactive	Active
Extreme pressure	fair	good	good	very good	low	fair
Antiwear	good	low	very good	low	good	poor
Reactivity	low	high	low	high	low	very high
Cu/corrosion	low	high	low	high	low	high
Antioxidant	good	low	good	poor	good	poor
Lubricity	fair	fair	very high	very high	poor	poor

performance can be observed. Straight sulfurized olefins are unpolar and show a relative poor affinity to metal surfaces (see the Polarity subsection of [Section 4.2.1](#) ahead). As the polarity increases from Olefin < Ester < Triglyceride, the EP performance increases in the same order. This behavior is demonstrated in a simple four-ball EP Test. Chart 1 shows the four-ball weld load (DIN 51350 Part 2) of sulfurized additives on the sulfur level in oil. The products with a high polarity (C,D) show considerably higher EP loads than the unpolar additives (A,B).

The content of active sulfur is only of minor importance on the EP performance, but the polarity and chemical structure play a major role.

Activity

Active sulfur is the amount of sulfur available for a reaction at a certain temperature. A common method for its determination is ASTM D-1662 [35]. The amount of active sulfur is determined by reacting copper powder with the sulfurized product for 1 hr at 149°C. Depending on the raw materials and the sulfurization method, the active sulfur content can vary very much. The activity is a function of the temperature. [Chart 2](#) shows typical active sulfur contents of sulfurized products based on different chemistry and sulfurization methods.

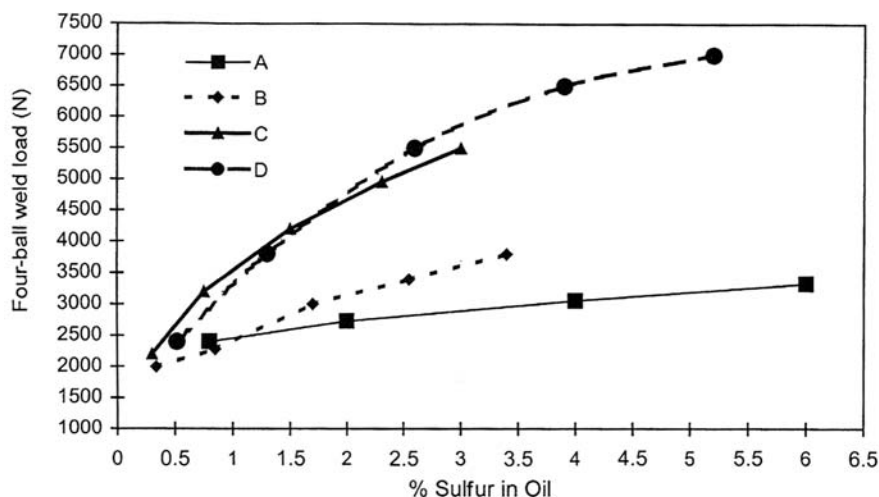
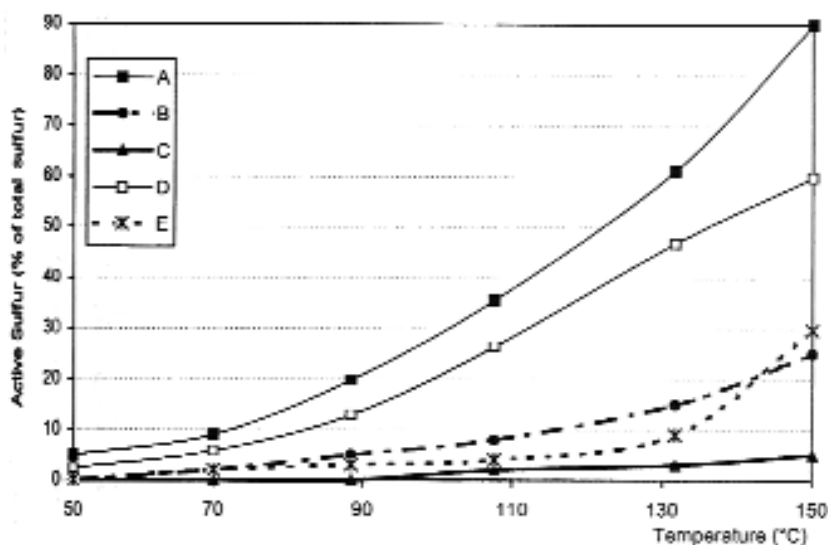


Chart 1 Influence of Raw Materials on EP Performance

Type	Total sulfur	Active sulfur	Activity (%)
A Olefin	40	36	90
B Ester	17	8	47
C Triglyceride	10	0.5	5
D Triglyceride	18	9	50



Type	Total sulfur	Active sulfur at 149°C
A Olefin	40	36
B Olefin	20	5
C Triglyceride	10	0.5
D Triglyceride	18	10.5
E Olefin/Triglyceride	15	4.5

The activity depends mainly on the sulfur chain in the molecule. Mono- and disulfides are not aggressive against yellow metals. Pentasulfides are highly reactive and, therefore, suitable for heavy-duty machining of steel. The inhibition of these products against yellow metals is hardly possible. Long-chain sulfur bridges in polysulfides (A) are thermally less stable than short sulfur bridges, where the sulfur is linked to the carbon atom of the raw material. For this reason, the reaction with the metal surface is possible at relatively low temperatures. Mono- and disulfides show only a medium activity, because the sulfur will be released only at higher temperatures [36]. The active sulfur at a given temperature is an indication on the ability of the product to provide sufficient reactive sulfur to form metal sulfides. Published work on the mechanism of the influence of organosulfur compounds on the load-carrying properties of lubricating oils indicates that this is due to their ability to form sulfide films which are more easily sheared than the metallic junctions under extreme-pressure conditions [37].

Therefore, active sulfur has a significant influence on the antiwear performance. Higher sulfur activity results in faster formation of the metal sulfide, and higher wear. This performance is visualized in [Chart 3](#). The chart shows the four-ball wear scar (DIN 51350 Part 3) of sulfurized products with various activity.

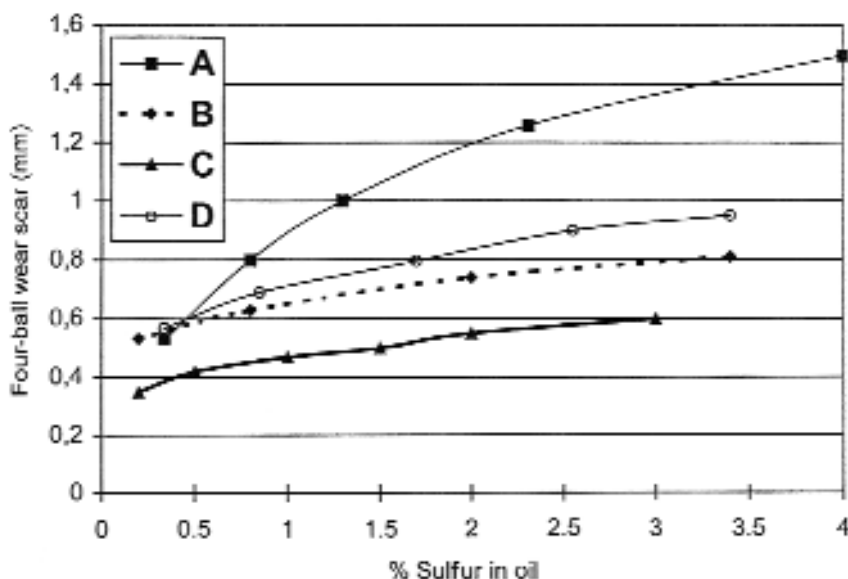


Chart 3 Influence on Activity on AW Performance

Type	Total sulfur	Active sulfur	Activity (ASTM D-1662) (%)
A Hydrocarbon	40	36	90
B Hydrocarbon	20	5	25
C Triglyceride	10	0.5	5
D Triglyceride	18	10.5	58

Copper Corrosion

ASTM D-130 [38] is a common method to determine the copper corrosion of additives. This copper corrosion does not necessarily reflect the activity of a sulfurized product, because very often, yellow metal deactivators are used to mask the active sulfur. The degree of copper corrosion depends on the amount of active sulfur and the presence of yellow metal deactivators. Inactive sulfurized products will show a long-term inactivity toward yellow metals, whereas active sulfur, masked with yellow metal deactivators, will react with the yellow metal as soon as the deactivator is consumed/reacted.

Therefore, the only statement that can be made is that a product will not stain copper under the given test parameters. This method is not suitable to determine the activity that is of major relevance for the performance of a sulfurized product.

Antioxidant

Sulfurized products with low active sulfur content are suitable to improve the antioxidant behavior of lubricants. This is particular important if hydrocracked, almost sulfur-free base fluids are used. During the synthesis of these oils, the natural sulfur (mainly heterocycles, inactive) is removed. The reintroduction of inactive sulfur

carriers improves the oxidation stability, especially in combination with other secondary antioxidants.

Lubricity

Lubricity can be described as friction reduction under low-pressure conditions. Under these conditions physical adsorbed lubricating films are effective (*see Polarity, under Section 4.2.1 ahead*). Inactive sulfurized triglycerides are widely used to improve the lubricity of a lubricant. In general, the lubricity of sulfur carriers increases with the polarity. Sulfurized olefin (no lubricity) < sulfurized ester (medium lubricity) < sulfurized triglyceride (high lubricity). Special products with enhanced lubricity are based on synergistic raw material blends such as triglyceride/long-chain alcohol, triglyceride/fatty acid, and triglyceride/olefin.

Color

The color of sulfurized compounds is mainly influenced by the production method and by virtue of the raw materials. Light color is not only a matter of “cosmetics” but also a quality feature. Light-colored products manufactured with high-pressure hydrogen sulfide processes or by mercaptan oxidation do not have unsaturated double bonds left, and, therefore, they show better oxidation stability in general.

4.2 Physical Properties

4.2.1 Effect of Additive Structure on Properties

Raw Materials

The selection of the raw materials and the production process determine the chemical structure of the compound. The physical properties of a sulfurized product depend on the chemical structure. An overview is given in Table 2.

Polymerization

During the sulfurization process the molecules of the raw materials are linked through sulfur. Depending on the structure of the raw material, two or more raw material molecules will be linked. Triglycerides like lard oil, soy bean oil, etc., do polymerize and form solid, rubberlike products if the polymerization is not controlled through chain terminators like esters or olefins, containing only one double bond. Olefins with only one double bond do not polymerize. Two molecules are linked by a sulfur chain where length depends on the production process. Esters behave in a similar way but due to varying amounts of multiple unsaturated compounds in natural esters, some polymerization takes place. Dark sulfurized products not only

Table 2 Physical Properties of Sulfurized Products

	Ester	Triglyceride	Olefin
Polymerization	low	high	very low
Solubility	good	fair-good	very good
Polarity	moderate	high	low
Viscosity	low	high	very low
Biodegradability	good	excellent	poor

show less oxidation stability compared to light-colored, fully saturated compounds, but also resume polymerization after the production process is finished.

Solubility

The solubility is mainly a function of the polarity of the product. As the polarity increases from olefin < ester < triglyceride, the solubility decreases. Polarity as well as the grade of polymerization determine the solubility. In general, sulfurized olefins have excellent solubility in solvents and all mineral oils. Depending on the sulfurization method, esters can exhibit good solubility even in Group II and Group III base oils if their polymerization grade is controlled during production. Sulfurized triglycerides are, in general, limited in their solubility due to their high polarity. But even more, the grade of polymerization plays a predominant role. A controlled reaction/polymerization can lead to light-colored products that will be soluble in paraffinic base oils, whereas uncontrolled polymerization will lead to dark-colored products, soluble only in oils with a higher polarity and aromatic content such as, for example, naphthenic base oils.

Polarity

Polarity determines the adhesion of a sulfurized product to the metal surface. The polarity depends on the raw materials used for the sulfurization. The organic portion of the molecule is responsible for the polarity and the affinity of the sulfurized product to the metal surface [36]. As the polarity increased from sulfurized hydrocarbon < sulfurized ester < sulfurized triglyceride, the affinity (physical adsorption) to metal surfaces increases also. Therefore, sulfurized products based on triglycerides, fatty acids, or alcohols provide superior lubricity compared to sulfur carriers based on less polar esters or nonpolar olefins.

Viscosity

Viscosity of a sulfurized product depends on the type of raw material used for the sulfurization and on the polymerization grade. A higher degree of polymerization (molecular weight) results in higher viscosity. The raw materials determine the viscosity index (VI) of a sulfur carrier. While short-chain sulfurized olefins show low VIs, sulfurized triglycerides can have viscosity indices above 200.

Biodegradability

Depending on the raw materials and on the sulfurization process, sulfurized products cover the whole range from not biodegradable to readily biodegradable. Besides the raw material, the production technology plays a predominant role. Catalysts used, impurities in the raw materials, and side components formed during the synthesis have a strong influence on the biodegradability. Therefore, biodegradability cannot be predicted but has to be tested for every single product. Biodegradable sulfur carriers are available for various applications [39].

Stability

Storage stability is obtained by total reaction of the double bonds in the sulfur carrier and in eliminating hydrogen sulfide and mercaptans. Especially mercaptans, but also hydrogen sulfide, are left over from the sulfurization process. If H_2S or mercaptans are not removed completely, they will evaporate under severe conditions in the final application or even under unfavorable storage conditions. Depending on

the raw materials and the type of sulfurization process, some sulfurized products continue to polymerize during storage. Especially triglycerides, sulfurized with flowers of sulfur under atmospheric pressure, show a steady and sometimes very strong polymerization during storage.

5 COMPARATIVE PERFORMANCE DATA IN PERTINENT APPLICATION AREAS

5.1 Metal Working

5.1.1 Cutting/Forming

In principle we have to deal in all cutting processes with abrasive wear (i.e., cutting) and adhesive wear (i.e., build-up edges). Depending on the particular process, respectively, the machining parameters of one of these wear types plays a dominant role. At low machining speeds, like in most of the forming operations, adhesive wear (cold welding), the formation of build-up edges and wear on the flank of the cutting edge are very often the limiting factor for tool life. At high machine speeds and increasing contact temperatures, the abrasive wear determines the tool life. The reactivity of additives depends on temperature and pressure. Field and laboratory tests showed that different types of sulfur carriers (same sulfur content but varying raw materials and/or production processes) lead to significantly different results in a metal-working operation [40].

5.1.2 Contribution of Sulfur Carriers to Metal Working

Sulfurized products can be designed to meet technical and ecological requirements in metal-working processes. They have been used successfully for more than 80 years to avoid abrasive and adhesive wear and enhance lubricity. In cutting operations their main function is to support the cut and to prevent wear of the tool, whereas in forming processes, sulfurized products should form a pressure-stable lubricant film and prevent adhesive wear.

5.1.3 Replacement of Sulfur Flowers

In the past it was very common to dissolve sulfur flowers in metal-working fluids to obtain a high reactivity and good extreme-pressure properties. This procedure is very cost-intensive because it has to be done under controlled temperature conditions below the melting point of sulfur and has many disadvantages like limited solubility (max 1% S), limited stability (sulfur dropout), and high corrosivity toward yellow metals. Also, there is a risk of H_2S generation, a highly toxic gas well known because of its rotten-egg odor. Today this process is widely substituted by using sulfurized products. If just reactivity is required, sulfurized olefins with high total and active sulfur content are used, though it is possible to adjust almost any activity/lubricity ratio while using a combination of appropriate sulfurized products.

5.1.4 Cu Corrosion

Depending on the process and on the metals machined, corrosion control toward yellow metals can be a requirement. If inactivity (no staining) toward yellow metals is required, it is important to use either absolute inactive sulfurized products or

medium-active sulfur carriers in combination with yellow metal deactivators. Active sulfurized products can be inhibited short term but will in the long term turn active again.

5.1.5 Substitutes for Chlorinated Paraffins

The driving forces for the replacement of chlorinated paraffins are mainly ecological and toxicological reasons. Users and waste oil disposal facilities have additional concerns over the corrosivity of the chlorinated paraffin decomposition products, primarily hydrochloric acid.

Chlorinated paraffins work because of their ability to form a highly persistent lubricating film even at low temperatures or moderate pressure. At high-temperature, high-pressure conditions, they decompose and the formed hydrogen chloride forms iron chloride with the metals involved in the process [40].

Chlorinated paraffins can be substituted by sulfurized products. Depending on the main function of the chlorinated compound in the particular process used, lubricity, or activity, suitable sulfurized products are available that can function as alternatives. The lubricity performance is mainly covered by highly polar, inactive sulfur compounds (see [lubricity](#)), whereas the activity will be covered by reactive sulfurized olefins or mixed sulfurized olefins/triglycerides.

5.1.6 Substitute for Heavy Metals

Heavy metals, particularly lead, antimony, molybdenum, and zinc compounds are used as extreme-pressure (EP) and antiwear (AW) additives in severe metal-working processes. Sulfur carriers have proven to be suitable substitutes, particular when used with synergistic compounds like polymer esters, phosphates, phosphites, dialkyldithiophosphates, and sulfonates.

5.1.7 Carbon Residue Reducing in Rolling Oils

Sulfur carriers are used in cold rolling of steel to prevent carbon residues built up on the surface of the metal sheets during the annealing process. Carbon residues are generated by oxidation/polymerization of additives used in rolling oils. Therefore, typical rolling oils contain sulfur-based antisnakey edge and carbon-reducing additives [41]. Clean burning of the lubricant is important to obtain a clean metal surface that can be evenly coated in subsequent process steps. Typical products used for this application are sulfurized olefins with low to medium activity.

5.1.8 Water-Miscible Metal-Working Products

Sulfurized products are used in water-miscible metal-working systems to provide extreme-pressure performance and, depending on the type of sulfur carrier, lubricity. By far the biggest applications are soluble oils or emulsions. Standard sulfurized products are not water-soluble. Surfactants must be used to keep the sulfur carrier in the emulsion. Compared to applications in nonwater-based systems, the water-based systems require hydrolytically stable products that can react at relative low temperature. Therefore, active sulfurized olefins, preferably pentasulfides, are widely used for this application. Sulfurized esters and triglycerides are also used, especially if additional lubricity is required. Specialty sulfur carriers are reaction products of sulfurized fatty acids and sulfurized hydrocarbons. These sulfur carriers combine good emulsifying properties with relative high hydrolytic stability and activity.

Straight sulfurized fatty acids, like sulfurized oleic acid, are used in semisynthetic metal-working fluids. The sulfurized fatty acid will be reacted with alkaline compounds like amines or potassium hydroxide to form a soap. This soap is water-dispersible and needs much fewer emulsifiers than a sulfurized olefin. However, hard-water stability can become a problem with this type of sulfur carrier.

5.2 Grease

High demands on load-carrying capacity of machine parts require the use of extreme-pressure and antiwear additives to avoid material loss and the destruction of the surfaces of the friction partners. Older technology still uses typical gear oil sulfur carriers based on short-chain olefins like isobutene. These sulfur carriers provide a high sulfur content, but their distinct, strong odor prohibits their use in open lubricating systems. As it is almost impossible to mask the activity of sulfurized products in greases by using yellow metal deactivators or sulfur scavengers, inactive sulfurized products are widely used as extreme-pressure additives in greases. Especially if the grease is designed for a wide application range, it is imperative that truly inactive sulfur carriers are used, because yellow metals are widely present as friction partners (e.g., brass cages in bearings). In addition, there are increasing demands on high-temperature stability for various grease types. This also calls for inactive, oxidation-stable sulfurized products. Typical sulfur carriers for greases are shown in Table 3.

Sulfurized products are also used to substitute heavy-metal-containing compounds, which are traditionally used as extreme-pressure additives in greases. Besides their excellent performance, these heavy-metal-containing compounds show some weak points. Antimony and bismuth compounds are known to have some weakness regarding copper corrosion, and lead compounds are toxic. In the meantime, many of these products have been replaced by special sulfurized products either as a direct replacement or in combination with synergistic compounds such as

Table 3 Typical Sulfurized Products for Greases

Type	Total sulfur	Active sulfur	Features
Triglyceride	8–12	0.5–3	Mainly inactive, limited EP performance
Triglyceride	13–15	4–7	Mainly active, hardly to mask Cu corrosion long term; good EP
Hydrocarbon	45	10–15	High EP performance, very distinct odor, only for encapsulated systems
Triglyceride/hydrocarbon	15	4	Mainly inactive, high EP performance
Ester	9–11	1–3	Mainly inactive, limited EP performance, excellent low-temperature pumpability

zincdialkyldithiophosphates, phosphate esters, or overbased sulfonates [42]. Sulfurized products are also used in greases for constant velocity joints (CVJ) [43]. They are very efficient in combination with molybdenum compounds [e.g., molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate (MoDTP), Mo-organic salts] as a sulfur source to support the formation of lubricating active molybdenum-di-sulfide in the friction zone.

There is an increasing demand for EP greases for environmentally sensitive applications like railroad wheel flange lubrication, railroad switches, and agricultural equipment like tractors or cotton picker spindles. Some sulfurized products are biodegradable and show excellent ecological data [40]. Therefore, these products are used rather than heavy-metal-containing compounds to enhance EP and AW properties in such applications.

5.3 Industrial Oils

An increasing variety of industrial fluids uses sulfurized products as EP and AW additives.

5.3.1 Industrial Gear Oils

Typical sulfur carriers for this application are short-chain sulfurized olefins. Sulfurized isobutene or diisobutene is widely used as an EP additive in industrial gear oils. Sulfurized isobutene has been used for decades as the EP additive of almost all industrial gear oil package. The high sulfur content, combined with a relative low active sulfur level, is ideally suited to match the requirements. Unfortunately, these products have a very distinct odor and, depending on the manufacturing process, can contain chlorine compounds. Newer developments are based on sulfurized olefins with a longer chain length. Speciality products with additional demands on lubricity are based on sulfurized triglycerides or mixtures of sulfurized olefins and triglycerides.

5.3.2 Slideway Oils

Slideway oils are a special type of gear oils with very good antistick-slip properties. Besides the austere requirements on coefficient of friction, there are also demands on compatibility and demulsibility with metal-working emulsions. Inactive sulfurized triglycerides are suitable to reduce the coefficient of friction. Unfortunately, most of these products are easy to emulsify and will, therefore, not meet the requirements on demulsibility without extensive formulation work. Modern slideway oils are based on demulsifying sulfurized hydrocarbon/triglyceride-based products that combine the advantage of a low coefficient of friction, good demulsibility, and high EP loads.

5.3.3 Hydraulic Fluids

It is possible to use inactive sulfur carriers in hydraulic systems with only moderate requirements on thermal stability. Typical products are sulfurized olefins and triglycerides or mixtures thereof.

5.3.4 Multifunctional Lubricants

Multifunctional lubricants cover more than just one lubrication application. There are increasing demands for this lubricant type, especially in metal-working shops. As one lubricant will be used for different applications with sometimes very different requirements, it is important that multifunctional additives are used. Depending on the overall performance requirements, sulfur carriers are used as EP, AW, or lubricity additives (see [Tables 1](#) and [2](#)). Multifunctional lubricants are almost always a compromise in their formulation. For example, metal-working machines with combined gear oil/process oil sump require fine-tuned additives, especially on the EP side. Sulfur carriers with a medium activity, additionally passivated with sulfur scavengers, are widely used for this application.

5.3.5 Agricultural Applications

Lubricants in agricultural applications can be spilled on soil either because of the machine design or because of leaks in hydraulic and gear systems. Therefore, there are increasing requirements on environmentally compatible or less harmful lubricants. Sulfurized products are ideally suited for this type of applications. They can be designed to meet performance and ecological requirements (e.g., biodegradability). A wide range of lubricants exists for outdoor equipment based on vegetable oils (e.g., soybean, canola, rape seed, and sunflower oils).

Sulfur carriers for these applications are mainly based on vegetable oils and synthesized in strictly controlled manufacturing processes. Typical sulfur carriers for agricultural applications are shown in [Table 4](#).

5.3.6 Automotive Applications

It is disclosed in U.S. Patents 4,394,276 and 4,394,277 that various sulfur-containing alkane diols may be formulated with lubricating oils to effectively reduce

Table 4 Sulfur Carriers for Agricultural Applications

Sulfur carrier type	Application
Ester, inactive	Gear greases (NLGI class 000), cotton picker spindle lubricants
Triglyceride, inactive	Gear lubricants, hydraulic fluids, greases for bearing lubrication, chassis lubricants
Triglyceride, medium active	Gear lubricants, chain saw and bar saw lubricants
Olefin, inactive	Gear greases (NLGI class 000), cotton picker spindle lubricants
Triglyceride/olefin, inactive	Gear lubricants, hydraulic fluids, greases for bearing lubrication, chassis lubricants

fuel consumption in an internal combustion engine. Sulfurized products, in general, and inactive sulfurized, oxidatively stable olefins, in particular, are known to reduce friction efficiently in engines. They provide not only antiwear and antifriction but also antioxidation properties. However, they cannot substitute the multifunctional zinc dialkyldithiophosphates in this application.

Besides crankcase applications, the use of sulfurized products in automotive gear lubricants is far more important. Since the middle of the 20th century, almost every gear lubricant for automotive applications has been formulated with sulfurized isobutene. The advantages of sulfurized isobutene are its high sulfur content, oxidation stability, and low corrosivity, but the very distinct odor and the low lubricity are disadvantageous.

Sulfurized esters and triglycerides are used in special transmission fluids to adjust the stick-slip properties. These sulfur carriers are also used in other lubricants in the automotive area such as wheel-bearing or constant velocity joint grease.

5.4 Synergies/Compatibility with Other Additives

Sulfurized products are compatible with most of the additives used in lubricants. Only strong acids and bases must be avoided in combination with sulfurized carriers.

5.4.1 ZnDTP

Zinc dialkyldithiophosphates are used in combination with sulfurized products in various applications. Besides their primary functions as antiwear and antioxidants, there is a well-known synergistic effect in regard to stabilization and improvement of copper corrosion of sulfur carriers. This behavior is demonstrated in the ASTM D-130 copper corrosion test (Table 5).

In addition, ZnDTP can have a very positive effect on the odor of sulfur carriers.

5.4.2 Basic Alkali Metal Salts

Sulfurized products show a very strong synergistic effect in combination with basic alkali metal salts [44], often referred to as overbased sulfonates or carboxylates. Particularly active sulfur in combination with overbased calcium or sodium sulfonates exhibits advantageous performance with regard to improved load-carrying and antiwear properties. These additive combinations are used in lubricants for severe metal-working operations.

Table 5 ZnDTP, Synergistic Effect on Copper Corrosion

Type	Total sulfur	Active sulfur	Treatment level (%)	Cu corrosion 3 h @ 100°C	+1.5% ZnDTP*	Cu corrosion 3 h @ 100°C
Triglyceride	18	10.5	5	4c		3b
Ester	17	8.5	5	3b		1b
Triglyceride	15	5	5	3a		1b

*Thermally stabilized zincdialkyldithiophosphate based on 2-ethylhexyl alcohol.

It is disclosed in international Patent WO 87/06256 [42] that the load-bearing characteristics of a grease composition and a gear lubricant may be unexpectedly improved by formulating these compositions with an additive mixture comprising overbased salts of alkaline earth metals or alkali metals and at least one sulfurized organic compound. From today's point of view the overbased products/sulfur combination has its advantages in some stainless steel cutting and forming operations. But the high alkalinity of such formulations shows big compatibility problems when in contact with lubricity esters and other types of acidic additives. Alkaline washing baths are used up quickly and need much more frequent changes as calcium soaps build up. Welding without cleaning the metal surface is also impossible as the high TBN sulfonates are generating high amounts of oxide ash.

5.4.3 Antioxidants

Inactive sulfur carriers show a synergism with aminic antioxidants. This effect is very distinct in low or even sulfur-free base fluids. Active sulfurized products do not show this synergy. In the contrary, the active types deteriorate the oxidation stability. Table 6 demonstrates the oxidation stability (ASTM D-2270, RBOT Test) of an active and inactive sulfur carrier based on the same raw materials.

The inactive product improves the oxidation stability (250 min), twice as much as the active type (120 min). In combination with the aminic antioxidants, the synergistic effect is obvious. While the inactive sulfur carrier improves the antioxidant (AO) properties of the aminic AO, the active type has a detrimental effect and reduces the oxidation stability.

5.4.4 Esters/Triglycerides

Esters are used either as base fluids or as additives. It is important to coordinate ester type and sulfur chemistry to achieve optimum performance. Unsaturated esters show strong synergistic effects with active sulfur, whereas inactive sulfur shows distinct synergies with saturated esters. The performance of sulfur carriers in saturated esters is similar to their performance in mineral oil. These synergies are widely used in the formulation of lubricants.

Combinations of active sulfur and unsaturated esters or triglycerides (mainly vegetable or animal oils like canola, rape seed, tall, sunflower oil, and esters thereof) are very common in all types of metal-working fluids, in oils as well as in water-based systems. The combination of these products shows better extreme-pressure and anti-wear properties than the single components. This performance is illustrated in the four-ball test (see Table 7).

Table 6 Antioxidant Properties, Influence on Oxidation Stability

	Base oil hydrocracked, dewaxed, no sulfur (min)	1.0% inactive hydrocarbon, 20% S, 5% active S (min)	1.0% active hydrocarbon, 39% S, 30% active S (min)
Base oil	40	250	120
0.2% Aminic AO (alkylated diphenylamine)	400	540	135

Table 7 Active Sulfur, Synergistic Effects with Unsaturated Esters

Sulfurized olefin 40% S, 36% active	TMP—Oleate	Four-ball weld load DIN 51350 part 2 (N)	Four-ball wear scar DIN 51350 part 3 (mm)
1.5%	—	2800	0.8
—	5.0%	800	0.6
1.5%	3.5%	3200	0.55

Other applications for the combination active sulfur/unsaturated ester are heavy-duty gear oils in agricultural applications and environmentally friendly chain saw and bar saw lubricants (see [agricultural applications](#)).

If Cu corrosion presents a problem, the use of medium-active sulfurized products in combination with unsaturated esters is of advantage. Some of these sulfur carriers are active enough to create the synergistic effects, but their Cu corrosion can be controlled with suitable yellow metal inhibitors.

Aside from the improvement of EP and AW performance, inactive sulfur carriers can boost the AO properties.

Saturated esters are used where good oxidation stability is required. The performance of sulfurized products in saturated esters is comparable to the performance in mineral oil. Inactive sulfur olefins and sulfurized triglycerides, and mixtures thereof, are typically used as additives in lubricants based on saturated esters.

5.5 Cost-Effectiveness

Sulfurized products cover the whole range from relative cheap commodity to high-price specialty. Depending on the type and treatment level, sulfurized products can be a major cost factor in lubricants. However, the use of sulfur carriers enables us to run processes and to overcome lubrication problems that cannot be solved in a cost-efficient way with other additives. For example, it is possible to increase machine speeds and thus productivity while using appropriate sulfur carriers instead of esters or chlorinated paraffins. Depending on the type of sulfur carrier, other commonly used additives in a formulation, for example esters or yellow metal deactivators, can be saved. In comparison with heavy-metal or chlorine-containing lubricants, the disposal costs for the used lubricant can be much lower.

Besides direct cost savings, respectively, cost efficiency due to higher productivity and lower disposal costs, there are secondary cost factors. In comparison to some traditionally used EP additives like chlorinated paraffins (HCl formation → rust), overbased sulfonates (difficult degreasability, incompatibility with other additives) or heavy-metal-containing additives (residue formation), sulfurized products show, in general, lower cost-effective side effects.

6 MANUFACTURE AND MARKETING ECONOMICS

6.1 Manufacturers

DAI Nippon Inc., Japan
Elco, USA

Atofina, France
Ethyl, USA
Ferro-Keil, USA
Harrison, Australia
Hornett, United Kingdom
Lubrizol, USA
Mayco, USA
Miracema, Brazil
Mobil Chemicals, USA
PCAS, France
Rhein Chemie, Germany

Additionally, some lubricant manufacturers still sulfurize dark-colored products for their own use, and some local sulfurization plants also sulfurize commodity-type products.

6.2 Marketers

In general, the manufacturers are also marketing the products. Some local manufacturers will buy sulfurized products and blend them with esters, mineral oil, etc. and sell them under their own brand name. Sulfur carriers are intermediates and not consumer products.

6.3 Economics

Market prices vary depending on the raw materials, the production process, and the performance level of the products. Low-quality, dark sulfurized fats with distinct odor and limited stability sell for less than USD 1.0 per kg. High-performance, top-quality, low-odor, light-colored products achieve prices of more than USD 4.0 per kg. Not only the raw materials, but much more the production process, determine the price for a sulfurized product. For example, the sulfurization of a typical gear oil sulfur carrier with di-sulfur-di-chloride and the necessary subsequent washing steps is more costly than the sulfurization of a fat with flowers of sulfur.

6.4 Government Regulations

6.4.1 Competitive Pressures

There are no government regulations concerning the use of sulfurized products, but depending on the location of the manufacturing plant very stringent regulations and conditions concerning emissions standards can apply. Therefore, there is a competitive distortion in production between more and less environmentally aware countries. Production technology and in particular low-emission production are key cost factors.

6.4.2 Product Differentiation

Apart from some commodities, there is a clear product differentiation mainly derived from quality and performance. A first criterion for differentiation is color, followed by sulfur content, raw materials, and odor. A classification is hardly possible because many of the products are tailormade either to cover a specific performance

profile or to meet specifications in various applications. A simple categorization by sulfur content or raw material bases would be too coarse and would not take performance into account. Even products based on the same raw materials but manufactured with a different process can be completely different in performance.

Modern, light-colored, high-performance products with low odor are sulfurized using hydrogen sulfide or mercaptans. Even the appearance distinguishes these products from conventionally sulfurized, dark-colored, smelly products.

7 OUTLOOK

7.1 Crankcase/Automotive Applications

Steady demands on reduction of phosphorus levels in motor oils as well as requirements for increased fuel efficiency, i.e. friction reduction, will open new opportunities for sulfur chemistry. Sulfurized products are already used in this type of application (see [section 5.3.6](#), automotive applications). New friction-reducing sulfurized products that remain to be tested are available.

7.2 Industrial Applications

Multifunctional and multipurpose lubricants are on the wish list of many end users. The development for sulfurized products that can be used in these types of lubricants is in full progress and products have already been commercialized. Mainly light-colored products based on mixed, well-balanced raw materials to ensure a broad performance range are used for multipurpose applications.

Replacement of heavy metals and chlorinated paraffins in almost all industrial lubricants is also an ongoing project widely found in the lubricants industry. Sulfur carriers play a predominant role as substitutes for these products.

Increasing demands for environmentally more acceptable lubricants has led many formulators into the development of lubricants based on natural triglycerides like canola oil, soybean oil, tall oil, or esters. Biodegradable sulfur carriers are used as extreme-pressure and antiwear additives as well as secondary antioxidants in these applications.

7.3 Current Equipment/Specification

Sulfurized products are single components and not complete performance packages such as, for example, hydraulic or crankcase packages. Therefore, sulfur carriers are used in the whole variety of lubricants rather than in a specific equipment. Also, no national or international specification standards exist for these products. The manufacturer sets the specification in agreement with the user.

7.3.1 Types of Equipment

As already mentioned, the biggest use of sulfurized products (excluding sulfurized isobutene) is in industrial applications. Metal-working and grease applications followed by industrial gear oils are formulated with sulfur carriers. A lot of old equipment is still in use. Many mid-size and small companies have not modernized their metal-working machines for more than three decades. This older, robust equipment is very often running at low machining speeds and at nonoptimized machining parameters.

7.3.2 Additives in Use

Today's additive usage depends very much on regional technological requirements and local legislation. In countries with low, old or standard technology and little environmental concerns, additives such as chlorinated paraffins or heavy metals are used for the formulation of lubricants, often in combination with sulfurized products. In countries where legislation has put some pressure onto the formulators and users of lubricants (higher disposal costs for chlorine-containing lubricants, limits on heavy metals in waste water, etc.), sulfurized compounds play an even more important role. They are the main extreme-pressure additives, very often combined with sulfonates, salicylates, phosphoric acid esters, dialkyldithiophosphates, or carboxylic esters to complement antiwear and lubricity performance.

7.3.3 Deficiencies in Current Additives

All available sulfur carriers are limited in their thermal stability. This is a desired feature, because reactive sulfur will only be released while the molecule breaks down. However, there are applications running at high temperature where a fast decomposition of the EP product is not desired. Corrosion toward yellow metals is another deficiency of sulfurized compounds. In high-temperature applications, the active sulfur will react with copper to form copper sulfide.

8. MEDIUM-TERM TRENDS

In general, there is a trend toward higher economy and ecological and toxicological safe lubricants.

8.1 Metal Working

Increased lubricant temperatures are a consequence of higher machine speeds, fully encapsulated machines, and reduced process steps. In the future, the thermal stability of metal-working lubricants and their toxicological safety will be the focus. Due to integrated applications (e.g., one lubricant for process and machine lubrication) the additives need to cover wide temperature ranges. The trend to replace multiple cutting steps with forming operations exists. Therefore, the type of additives will also change. Minimum-amount lubrication requires new lubricant concepts regarding performance and marketing. Maintenance of lubricants will further be reduced. Again, this trend calls for increased stability of additives.

Sulfurized products for metal-working applications will need improved thermal stability in combination with good solubility in high paraffinic or even synthetic base fluids. Ecological and toxicological safety will be basic requirements. Improved lubricity and excellent compatibility with process materials such as cleaners and paints will be essential for the formulation of modern lubricants for deformation processes (e.g., cold forging, deep drawing, etc.).

8.2 Industrial Oils

Synthetic fluids such as polyalphaolefins (PAO), polyalkyleneglycols (PAG), extra-high VI mineral oils (XHVI), or synthetic esters are being used in increasing volumes for the formulation of high-performance industrial lubricants. Smaller lubricant

sumps, reduced sizes of components, and increased performance will place high demands on the lubricants. Especially in mobile equipment (e.g., excavator, lawn-mower, etc.), ecological and toxicologically harmless lubricants will be in demand. Reduced maintenance and longer lubricant change intervals require high lubricant stability. Improved thermal stability, low copper corrosion, and excellent solubility in synthetic fluids are demands on sulfurized products for the new generation of industrial lubricants.

REFERENCES

1. H. Sellei. Sulfurised extreme-pressure lubricants and cutting oils, part 1. *Petroleum Processing* 4:1003–1008, 1949.
2. H. Sellei. Sulfurised extreme-pressure lubricants and cutting oils, part 2. *Petroleum Processing* 4:1116–1120, 1949.
3. Base for metal-cutting compounds and process of preparing the same. U.S. Patent 1,367,428, German Patent 129132 (1921, GW Pressell, Houghton & Co.).
4. JT Byers. Patents show trend in extreme pressure lube technology. *National Petroleum News* 28:79, 1936.
5. MG van Voorhis. 200 lubricant additive patents issued in 1938 and 1939. *National Petroleum News*, 32:R-66, 1940.
6. FL Miller, WC Winning, JF Kunc. Use of additives in automotive lubrication. *Refiner and Natl. Gas Manuf.* 20(2):53, 1941.
7. HE Westlake, Jr. The sulfurisation of unsaturated compounds. *Chem Rev* 39(2):219, 1946.
8. FF Musgrave. The development and lubrication of the automotive hypoid gear. *J Inst Petr* 32(265):32, 1946.
9. Base for metal-cutting compounds and process of preparing the same. U.S. Patent 1,367, 428, G.B. Patent 129132 (1921, GW Pressell, Houghton & Co.).
10. Lubricating compound and process of making the same. U.S. Patent 1,974,299 (1934, LA Churchill).
11. Method of sulfurizing pine oil and data thereof. U.S. Patent 2,012,446 (1935, MC Edwards, J Heights, JV Congdon).
12. Method of sulfurizing terpenes, abiethyl compounds, etc. U.S. Patent 2,111,882 (1938, JW Borglin, Hercules Powder Company).
13. Pure compounds as extreme-pressure lubricants. U.S. Patent 2,110,281 (1938, EW Adams, GM McNulty, Standard Oil Company).
14. Production of mercaptanes. U.S. Patent 2,116,182 (1938, K Baur, IG Farbenindustry AG).
15. Sulfurized oils. U.S. Patent 2,113,810 (1938, BH Lincoln, WL Steiner, Continental Oil).
16. Lubricating oil. U.S. Patent 2,164,393 (1939, EA Evans, CC Wakefield & Co Ltd.).
17. Extreme pressure lubricating composition. U.S. Patent 2,020,021 (1935, BB Farrington, RL Humphreys, Standard Oil Company).
18. Lubricant composition. U.S. Patent 2,206,245 (1940, EW Adams, GM McNulty, Standard Oil Company).
19. Lubricating oil. U.S. Patent 1,971,243 (1934, JF Werder).
20. Lubricant containing organic sulfides. U.S. Patent 2,205,858 (1940, LA Mikeska, FL Miller, Standard Oil Development Company).
21. Compounded lubricating oil. U.S. patent 2,422,275 (1947, C Winning et al. Standard Oil Development Company).
22. HC Mougay, GO Almen. Extreme pressure lubricants. 12:76, IBID 1931.

23. JP Baxter et al. Extreme pressure lubricant tests with pretreated test species. *J Inst Petr* 25(194):761, 1939.
24. H Schallbock et al. Vorträge der Hauptversammlung der deutschen Gesellschaft für Metallkunde. VDI Verlag, 1938, pp 34–38.
25. CF Prutton et al. Mechanism of action of organic chlorine and sulfur compounds in E.P. lubrication. *J Inst Petr* 32:90–118, 1946.
26. Lubricant. U.S. Patent 2,179,067 (1939, HG Smith, Wallingford, PA, Gulf Oil Corporation).
27. Lubricant. U.S. Patent 2,311,931 (1943, EW Cook, WD Thomas, American Cyanamid Company).
28. ES Forbes. Load carrying capacity of organo-sulfur compounds—a review. *Wear* 15:341, 1970.
29. Process for producing sulfurized olefins. U.S. Patent 3,703,504 (1972, AG Horodysky, Mobil Oil Corporation).
30. A sulfurised mixture of compounds and a process for its production. German Patent 1,371,949 (1972, I Kreutzer, Rhein Chemie Rheinau GmbH).
31. Cross-sulfurized olefins and fatty monoesters in lubricating oils. U.S. Patent 4,053,427 (1977, BW Hotten, Chevron Research Company).
32. Metal working using lubricants containing basic alkali metal salts. U.S. Patent 4,505,830 (1985, JN Vinci, The Lubrizol Corporation).
33. Prof. Hugo, Freie Universität Berlin, Rhein Chemie Rheinau GmbH Internal Studies, 1980.
34. J Korff. Additive fuer Kuehlschmierstoffe. Additive fuer Schmierstoffe. Expert Verlag, 1994.
35. ASTM D 1662, Standard test method for active sulfur in cutting oils.
36. A Fessenbecker, T Rossrucker, E Broser, Rhein Chemie Rheinau GmbH—performance and ecology, two inseparable aspects of additives for modern metalworking fluids. TAE, 1992.
37. KG Allum, JF Ford. The influence of chemical structure on the load carrying properties of certain organo-sulfur compounds. *J Inst Petr* 51(497), 1965.
38. ASTM D-130, Detection of copper corrosion from petroleum products by the copper strip tarnish test.
39. I Roehrs, T Rossrucker. Performance and ecology—two aspect for modern greases. NLGI Annual Meeting, 1994.
40. T Rossrucker, Dr. A Fessenbecker. Performance and mechanism of metalworking additives: New results from practical focused studies. Rhein Chemie Rheinau GmbH, STLE Annual Meeting, 1999.
41. J Deodhar, Steel rolling oils—cold rolling lubrication. The metalworking fluid business, The College of Petroleum Studies, Dec. 1989.
42. JN Vinci. Grease and gear lubricant compositions comprising at least one metal containing composition and at least one sulfurized organic compound. The Lubrizol Corporation, OH, International Publication no. WO 87/06256, 1987.
43. Greases. WO 94/11470, Eur. Patent 0668 900 B1 (1994, G Fish, GKN Technology Limited).
44. Metal working using lubricants containing basic alkali metal salts. U.S. Patent 4,505,830 (1985, JN Vinci, The Lubrizol Corporation).

Olefin Copolymer Viscosity Modifiers

MICHAEL J. COVITCH

The Lubrizol Corporation, Wickliffe, Ohio, U.S.A.

1 INTRODUCTION

Olefin copolymer (OCP) viscosity modifiers are oil-soluble copolymers comprising ethylene and propylene and may contain a third monomer, a nonconjugated diene, as well. By virtue of their high thickening efficiency and relatively low cost, they enjoy a dominant share of the engine oil viscosity modifier market [1]. First introduced as a lubricant additive by Exxon in the late 1960s, the chemical and physical properties of OCPs continue to evolve to achieve improvements in low-temperature rheology, thickening efficiency, and bulk-handling characteristics.

Several excellent reviews of OCP viscosity modifiers have been published [1–3]. This chapter serves as an update and current compilation of information relating to the chemistry, properties, and performance characteristics of this important class of lubricant additives.

2 CLASSES OF OLEFIN COPOLYMERS

There are many ways to classify olefin copolymer viscosity modifiers. From a user's perspective, OCPs are marketed as either solids or liquid concentrates. The physical state of the solids depends on several factors, primarily the ethylene/propylene mass ratio (E/P). When the E/P is in the 45/55 to 55/45 range, the material is amorphous and cold-flows at room temperature. Thus, OCPs of this composition are most commonly sold as bales, packaged in rigid boxes to maintain bale shape. When the E/P is higher than 60/40, the copolymer becomes semicrystalline in nature and does not cold-flow under ambient conditions. Thus, both bales and pellets can be produced.

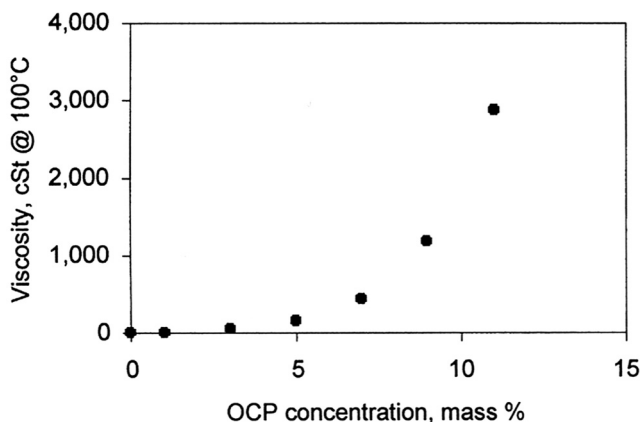


Figure 1 Kinematic viscosity of 50 PSSi amorphous OCP in 100N mineral oil.

Liquid concentrates of OCP in mineral oil contain enough rubber to raise the kinematic viscosity into the 500–1500 cSt (mPa·s) range at 100°C. A typical viscosity/concentration relationship is shown in Figure 1.

From the preceding discussion, OCPs can also be classified according to crystallinity, which is measured by X-ray diffraction or differential scanning calorimetry. The influence of crystallinity on rheological performance is discussed in Section 5.

Shear stability is another parameter by which OCP viscosity modifiers are categorized. The higher the molecular weight of a polymer, the more prone it is to mechanical degradation when elongational forces are imposed by the fluid flow field. This subject is dealt with in detail in Section 5.2.3.

Finally, chemical functional groups can be grafted to the OCP backbone, providing added dispersancy, antioxidant activity, and/or low-temperature viscosity enhancement. A number of chemical routes for functionalizing OCPs are described in Section 3.3.

3 CHEMISTRY

3.1 Synthesis by Ziegler-Natta Polymerization

Although methods for synthesizing high-molecular-weight polymers of ethylene were commercialized in the 1930s (the ICI high-pressure process), the polymers contained a significant number of short- and long-chain branches, which limited the ability to produce high-density polyethylene. The first commercially viable synthesis of linear polyethylene at low monomer pressure was pioneered by Ziegler in 1953, and the stereoregular polymerization of α -olefins was demonstrated by Natta the following year [4]. The secret to their success was the discovery of catalysts (called Ziegler or Ziegler-Natta catalysts), which are molecular complexes between halides and other derivatives of Groups IV–VIII transition metals (Ti, V, Co, Zr, Hf) and alkyls of Groups I–III base metals. A typical catalyst of this type comprises an aluminium alkyl and a titanium or vanadium halide having the general structure shown in Figure 2. Electron donors, such as organic amines, esters, phosphines, and ketones, may be used to enhance reaction kinetics. Finally, molecular-weight control is often

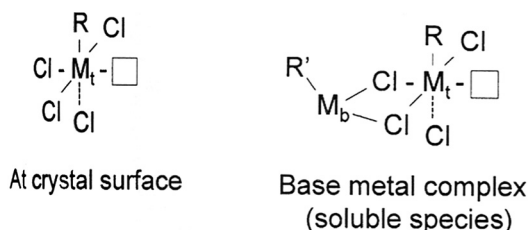


Figure 2 Active center in Ziegler–Natta catalysts. M_i = transition metal (such as Ti); M_b = base metal (such as Al). (From Ref. 4.)

aided by the use of chain transfer agents such as molecular hydrogen or zinc alkyls [5], which are effective in terminating chain growth without poisoning the active metal center.

Ziegler-Natta polymerization is probably the best-known example of insertion, coordination, and stereoregular or stereospecific polymerization. This nomenclature has been adopted to describe the mechanism(s) by which olefin monomers insert into the growing polymer chain, as directed by both steric and electronic features of the coordination catalyst. A commonly accepted chain propagation mechanism involves monomer insertion at the transition metal-carbon bond [4]. The main purpose of the base metal alkyl is to alkylate the transition metal salt, thus stabilizing it against decomposition. As pointed out by Boor [4], Ziegler-Natta catalysts may be modified to produce copolymers with varying degrees of randomness or, from a different perspective, blockiness of one or both co-monomers. Due to the higher reactivity ratio of ethylene to that of propylene [4–7], the formation of long runs of ethylene is more favored than long sequences of propylene. This is substantiated by ^{13}C NMR spectroscopy [8–13].

Ziegler–Natta catalysts come in two forms—heterogeneous and homogeneous. Heterogeneous catalysts are insoluble in the reaction medium and are suspended in a fluidized-bed configuration. Reaction takes place at the exposed faces of the metal complex surface. Since each crystal plane has a slightly different atomic arrangement, each will produce slightly different polymer chains in terms of statistical monomer insertion and molecular-weight distribution. Thus, they are often called multisite catalysts. Homogeneous Ziegler–Natta catalysts are soluble in the reaction solvent and, therefore, function more efficiently since all molecules serve as potential reaction sites. Since the catalyst is not restrained in a crystalline matrix, it tends to be more “single-site” in nature than heterogeneous catalysts. Polymers made by homogeneous polymerization generally are more uniform in microstructure and molecular-weight distribution and, therefore, are favored for use as viscosity modifiers [1,4].

Nonconjugated dienes are often used in the manufacture of ethylene propylene copolymers to provide a site for cross-linking (in nonlubricant applications) or to reduce the tackiness of the rubber for ease of manufacture and handling. Certain dienes promote long-chain branching [2,5,14,15], which, in turn, increases the modules in the rubber plateau region. The terpolymer is then easier to handle as it is dried and packaged [1]. A disadvantage of long-chain branching is that it reduces the lubricating oil thickening efficiency relative to a simple copolymer of similar molecular weight and copolymer composition, although low levels of vinyl norbornene or

norbornadiene are claimed [15] to improve cold flow without loss in thickening efficiency or shear stability.

3.2 Synthesis by Metallocene Polymerization

The desire to achieve higher levels of control over stereoregularity, composition, and molecular-weight distribution led to the development of activated metallocene catalysts. Although known to Ziegler and Natta, the technology was rediscovered by Kaminsky and Sinn in 1980 and further developed by workers such as Brintzinger, Chien, Jordan, and others [16–20]. Metallocene catalysts consist of compounds of transition metals (usually Group IVB:Ti, Zr, Hf) with one or two cyclopentadienyl rings attached to the metal. The most common activator is methylaluminoxane (MAO). A large number of variants have been reported, but the highest levels of stereospecificity have been achieved with bridged, substituted bis-cyclopentadienyl metallocenes (Figure 3). One of the major advantages of metallocenes over Ziegler–Natta catalysts is the ability to incorporate higher α -olefins and other monomers into the ethylene chain.

The first commercial use of metallocene single-site catalysts to manufacture EPDM elastomers was DuPont Dow Elastomers' Plaquemine, LA, facility, which began operation in 1996 using Dow's Insite® constrained geometry catalyst [22,23]. The catalyst is described as "monocyclopentadienyl Group 4 complex with a covalently attached donor ligand requiring activation by strong Lewis acid systems [such as] MAO." Several advantages of this technology over conventional Ziegler–Natta processes were reported. Since the catalyst is highly efficient, less is needed; therefore, the process does not require a metals removal or de-ashing step. In addition, the copolymers produced by this chemistry are reported to have narrow molecular-weight distributions for good thickening efficiency and shear stability as well as good control over copolymer microstructure. Metallocene-catalyzed polyolefins also differ from Ziegler–Natta polymers in that the former contains a predominance of unsaturated ethylidene end groups [24].

3.3 Functionalization Chemistry

Traditionally, olefin copolymers are added to lubricating oil to reduce the degree to which viscosity decreases with temperature, i.e., to function solely as a rheology

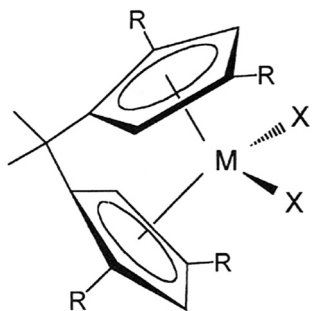


Figure 3 Chemical structure of generalized bridged bis-cyclopentadienyl metallocene catalyst. M is a Group IVB transition metal; X is a halogen or alkyl radical. (From Ref. 21.)

control agent. Other lubricant additives—such as ashless succinimide dispersants, a variety of antioxidants, detergents, antiwear agents, foam inhibitors, friction modifiers, and anticorrosion chemicals—provide other important functions (dispersing contaminants, keeping engines clean, maintaining piston ring performance, preventing wear, etc.). It has been recognized for many years that it is possible to combine some of these performance and rheology control features on the same molecule. Some report that “both dispersant and antioxidant functionality may exhibit more potent activity when attached to the polymer backbone than in their monomeric form” [25]. Three hybrids have been commercialized, although many more have been disclosed in the patent literature. They include dispersant OCPs (DOCP), dispersant antioxidant OCPs (DAOCP) and polymethacrylate-grafted OCPs (gOCPs). The addition of antiwear functionality has also been reported [25,26].

Although many grafting reactions have been described in the literature, two general classes have received the most attention. Free-radical grafting of nitrogen-containing monomers or alkylmethacrylates onto the OCP molecule is one class. Nitrogen-containing monomers such as vinyl pyridines, vinylpyrrolidinones, and vinylimidazoles are often cited in the parent literature [36]. Free-radical grafting with phenothiazine is claimed [27] to provide antioxidant functionality as well. The grafting reaction may be conducted with the OCP molecule dissolved in mineral oil or another suitable solvent; alternately, solvent-free processes have been disclosed [27] in which the reaction is conducted in an extruder.

Mixtures of alkylmethacrylate monomers, which are typical of those found in PMA viscosity modifiers, may be grafted to OCPs [28] to provide improved low-temperature properties. Adding nitrogen-containing monomers to the alkylmethacrylate mixture provides dispersancy characteristics as well. A common side reaction is homopolymerization, which can be minimized by process optimization. Homopolymers of N-containing monomers are usually not very soluble in mineral oils and often lead to hazy products and can attack fluoroelastomer seals. Homopolymers of alkylmethacrylates are fully soluble in oil, however. Thus, optimizing the grafting process is much more critical when working with N-containing monomers.

A second class of grafting reactions involves two steps [25,29]. In the first step, maleic anhydride or a similar diacyl compound is grafted onto the OCP chain, assisted by free-radical initiators, oxygen [45], and/or heat. In the second step, amines and/or alcohols are contacted with the anhydride intermediate to create imide, amide, or ester bonds. In many respects, this chemistry is very similar to that used to create ashless succinimide dispersants. An advantage of this approach over free-radical monomer grafting is that homopolymerization is avoided. The patent literature describes a related functionalization process in which free primary or secondary nitrogens of highly basic succinimide dispersants may be used to couple preformed dispersants to the maleic-anhydride-grafted OCP molecule [31]. Amine derivatives of thiadiazole, phenolic [25], and amino-aromatic polyamine [32] compounds have been reacted with maleic-anhydride-grafted OCP to provide enhanced antioxidant character to the additive [25].

Although maleic anhydride is the most common chemical “hook” for attaching functional groups to OCP polymers, a number of other approaches have been reported [33]. Further elaboration is beyond the scope of this review. Another approach for attaching functionality to the OCP chain is via the nonconjugated diene in the terpolymer [26,34]. For example, 2-mercapto-1,3,4-thiadiazole is

attached to the ethylenenorbornene site on an EPDM polymer via addition of the thio group across the ethylidene double bond. The thiadiazole group is claimed to provide antiwear, antifatigue characteristics to lubricants containing the grafted OCP.

4 MANUFACTURING PROCESSES

Two polymerization processes have been used for the manufacture of ethylene-propylene copolymer viscosity modifiers: solution and slurry. In the solution process, the gaseous monomers are added under pressure to an organic solvent such as hexane, and the polymer stays in solution as it forms. By contrast, the slurry or suspension process utilizes a solvent such as liquid propylene in which the resultant copolymer is not soluble. It is reported [35] that removing the catalyst residue from the polymer is more difficult in the slurry process, although some contend [36] that the levels of catalyst are so low that catalyst removal is not necessary.

Ethylene-propylene rubber was reported [37] to have been successfully manufactured in a fluidized-bed gas-phase reactor. However, the use of fluidization aids such as carbon black is necessary to process low-molecular-weight grades typical of lubricating oil viscosity modifiers. Thus, the gas-phase process is not appropriate for manufacturing OCP viscosity modifiers.

4.1 Solution Process

The most common method for manufacturing OCP viscosity modifiers is the solution process described in Figure 4. It is made up of four sections—polymerization, polymer isolation, distillation, and packaging. In the polymerization section, monomers, an organic solvent such as hexane, and the soluble catalyst are introduced into a continuously stirred polymerization reactor. During polymerization, the polymer remains in solution and causes the bulk viscosity of the reaction medium to increase. To maintain good agitation, monomer diffusion, and thermal control, polymer concentration in the polymerization reactor is typically limited to 5–6 weight% [36]. Up to five reactors arranged in series have been reported in the literature [39]. The effluent from the last reactor is contacted with an aqueous short-stop solution to terminate polymerization and wash away the catalyst, although this step is often omitted when using metallocene catalysts due to their high reactivity and, therefore, low concentration [22]. While the copolymer is still in solution, extender oils or antioxidants can be added.

In the isolation section, three techniques have been described in the literature. In the most common method (shown in Figure 4), the polymer is flocculated with steam, and the solvent and unreacted monomers are recovered, purified, and recycled. The aqueous polymer slurry is mechanically dewatered, granulated, and air-dried. A second, nonaqueous method for isolating the polymer has been described in which the polymer is concentrated in a series of solvent removal steps [40,41]. The final step may be conducted in a devolatilizing extruder. A third technique does not isolate the polymer as a solid; rather, it mixes the polymer solution into mineral oil and distills off the solvent, producing a finished liquid OCP product [2].

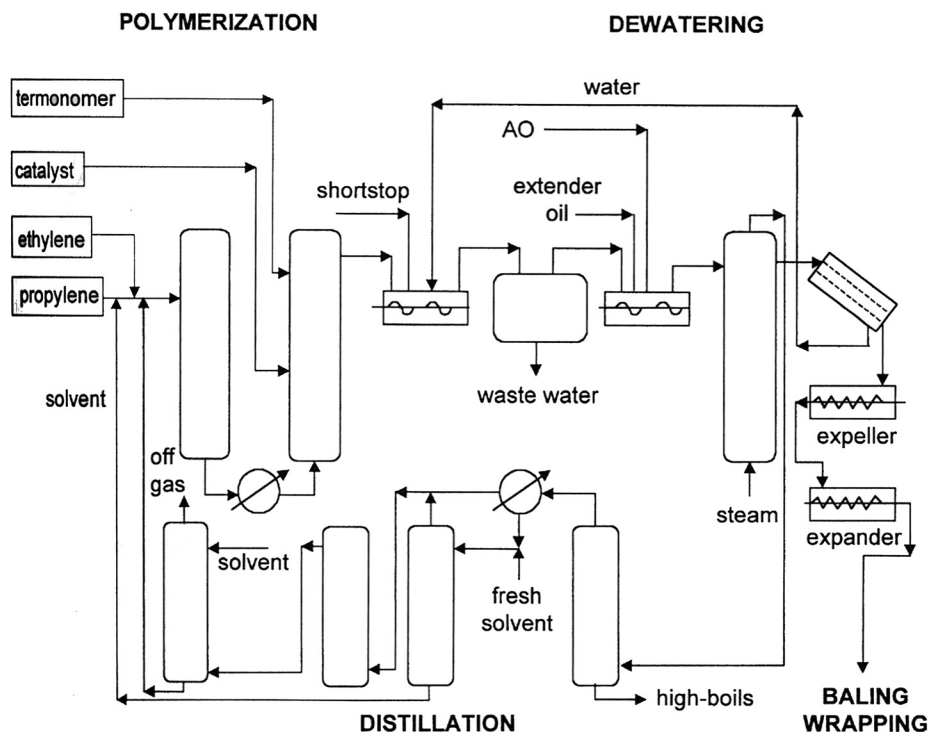


Figure 4 Solution process for manufacture of EPDM. (From Ref. 38.)

Another type of solution polymerization process that has received a great deal of attention has been Exxon's tubular reactor technology. Its purpose is to generate a polymer with long blocks differing in monomer composition for improved performance as a viscosity-improving polymer [3,42]. A schematic of this process is shown in Figure 5. Monomers and solvent are premixed with a highly active Ziegler-Natta polymerization catalyst and metered into a plug flow reactor under conditions that minimize chain transfer and termination reactions. Ethylene and/or propylene are injected into the tube at different points to adjust the local monomer concentration and, thereby, the monomer composition along the growing polymer chain. In comparing the rheological properties of different A-B-A-type block compositions, Ver Strate and Struglinski reported [3] that "chains with high ethylene section in the center of the chain associate at low temperature with little intermolecular connectivity." When the high-ethylene (crystallizable) segments are at the ends, polymer networks can form at low temperatures, which can impart a gelatinous texture to the solution.

4.2 Suspension Process

Ethylene and a nonconjugated diene, if desired, are contacted with liquid propylene, which acts as both a monomer and the reaction medium [36,43]. In the presence of a suitable catalyst, polymerization takes place rapidly, producing a suspension of

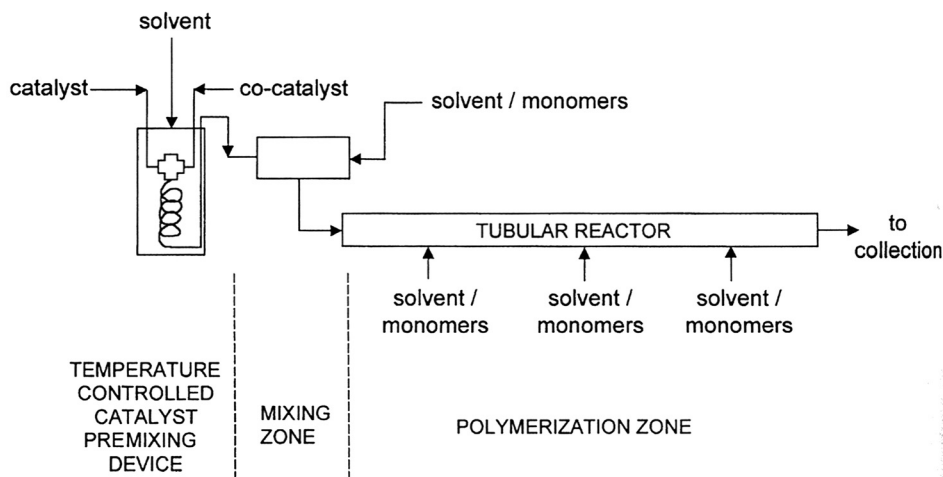


Figure 5 Tubular reactor process for preparation of multiblock ethylene/propylene copolymers. (From Ref. 42.)

copolymer granules that are insoluble in the reaction medium. The heat liberated during the polymerization reaction is dissipated by propylene evaporation, thus providing a convenient mechanism for temperature control. In addition, since the polymer is not soluble in the reaction medium, viscosity remains low. Thus, relative to typical solution processes, the polymer concentration in a suspension reactor can be five to six times higher. Upon exiting the polymerization reactor, the polymer suspension is contacted with steam to strip off unreacted propylene, which is then recycled. According to Corbelli and Milani [43], the Dutral[®] process does not include a catalyst-washing step. The copolymer product, in aqueous suspension, is dewatered, dried, and packaged in a similar fashion to polymer made by the solution process.

4.3 Postpolymerization Processes

Two main types of packaging processes are in practice today [37]. In one, the isolated polymer is mechanically compressed into rectangular bales. The bales are often wrapped in a polyolefin packaging film to prevent them from adhering to one another during storage and to prevent foreign matter from sticking to the tacky rubber surface. Typical types of polyolefins films include poly(ethylene-co-vinyl acetate), low-density polyethylene, and ethylene/ α -olefin copolymers. Another method for packaging solid OCP rubber is to extrude the polymer, pass the melt stream into a water-cooled pelletizer, and dry the final product. The pellets may be packaged in bags or boxes or may be compressed into rectangular bales.

The mechanical properties of the rubber often dictate what type of isolation and packaging processes are the most appropriate. Amorphous ethylene/propylene copolymers are often too sticky to successfully traverse the conventional floccula-

tion/drying/baling process. One way to modify these compositions to improve their handling characteristics is by introducing long-chain branching [5,44,45] through the use of low concentrations of nonconjugated dienes or other branching agents. For nonfunctionalized OCPs, this is the main reason some commercial viscosity modifiers contain dienes [2]. Copolymer compositions higher in ethylene content (>60 weight % [5]) are often semicrystalline and may be amenable to packaging in pellet form. In some cases, the pellets may contain an anticaking or antiblocking agent to prevent agglomeration.

Another type of manufacturing process has been used to manufacture low-molecular-weight OCP viscosity modifiers that are difficult to isolate and package in conventional equipment. A higher-molecular-weight feedstock of the appropriate composition may be fed into a masticating extruder or Banbury mixer to break down the polymer chain to lower-molecular-weight fragments using a combination of heat and mechanical energy [46]. Several patents describe the use of oxygen [47] or free-radical initiators [48] to enable this process.

4.4 Making the OCP Liquid Concentrate

After the solid OCP viscosity modifier has been manufactured, it must be dissolved in oil before it can be efficiently blended with base stocks and other additives. The first stage entails feeding the rubber bale into a mechanical grinder [2] and then conveying the polymer crumb into a high-quality diluent oil that is heated to 100–130°C with good agitation. The rubber slowly dissolves, raising the viscosity of the oil, as shown in [Figure 1](#). Certain high-intensity homogenizers can also be used in which the entire rubber bale is fed directly into a highly turbulent diluent oil tank at high temperature; this bypasses the pregrinding step.

When the solid polymer is supplied in pellet form, the rubber can be fed directly into hot oil; or, if it is slightly agglomerated, it first may be passed through a low-energy mechanical grinder.

5 PROPERTIES AND PERFORMANCE CHARACTERISTICS

5.1 Effect of Ethylene/Propylene Ratio on Physical Properties of the Solid

The co-monomer composition of ethylene/propylene copolymers has a profound influence on the physical properties of the rubber. These properties, in turn, dictate the type of containers in which the product can be stored and how it is handled during distribution and used.

¹³C NMR has been used extensively to characterize the sequence distribution of ethylene-propylene copolymers [8–13,53]. As the ratio of ethylene to propylene (E/P) increases, the fraction of ethylene-ethylene sequences (dyads) rises, as demonstrated by the data in [Figure 6](#). Concurrently, the total fraction of ethylene-propylene dyads decreases (forward and reverse propylene insertion are designated *p* and *p**, respectively). Thus, the average length of contiguous ethylenes increases with ethylene content. Above about 60 weight % ethylene, these sequences become long enough to crystallize, as measured by differential scanning calorimetry ([Figure 7](#)) or X-ray diffraction.

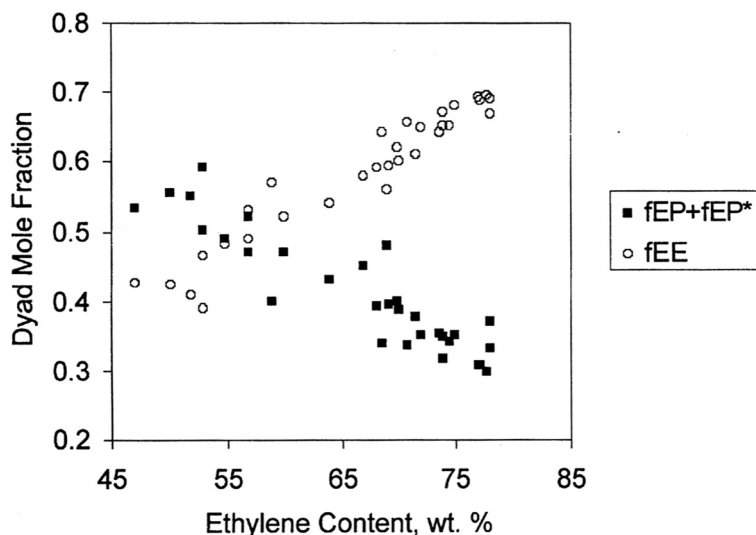


Figure 6 The effect of ethylene content (weight % as measured by NMR) on ethylene-ethylene (EE) and ethylene-propylene (EP) dyad concentration.

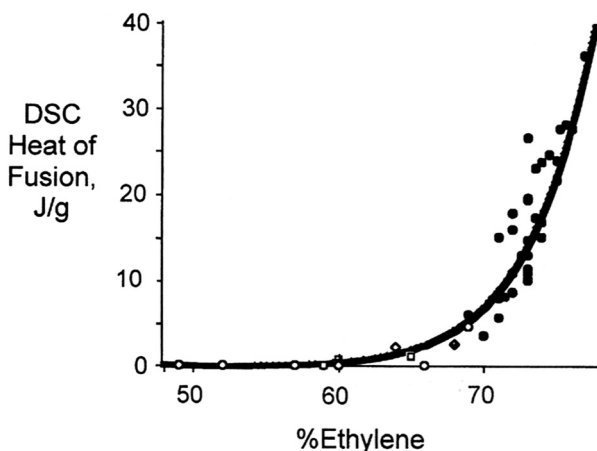


Figure 7 The effect of ethylene content (weight %) on crystallinity as measured by differential scanning calorimetry (DSC) for a range of experimental EPDM copolymers.

When the degree of crystallinity exceeds about 25%, ethylene-propylene copolymers become unsuitable as viscosity modifiers due to limited solubility in most mineral oils. As the propylene content approaches zero, the copolymer takes on the physical characteristics of high-density polyethylene, which, due to its inertness to oil, is used as the packaging material of choice for engine oils and other automotive fluids. Microstructural investigations of metallocene ethylene/ α -olefin copolymers by Minick et al. [50] concluded that the relatively short ethylene sequences of low-crystallinity (<25%) samples are capable of crystallizing into fringed micelle

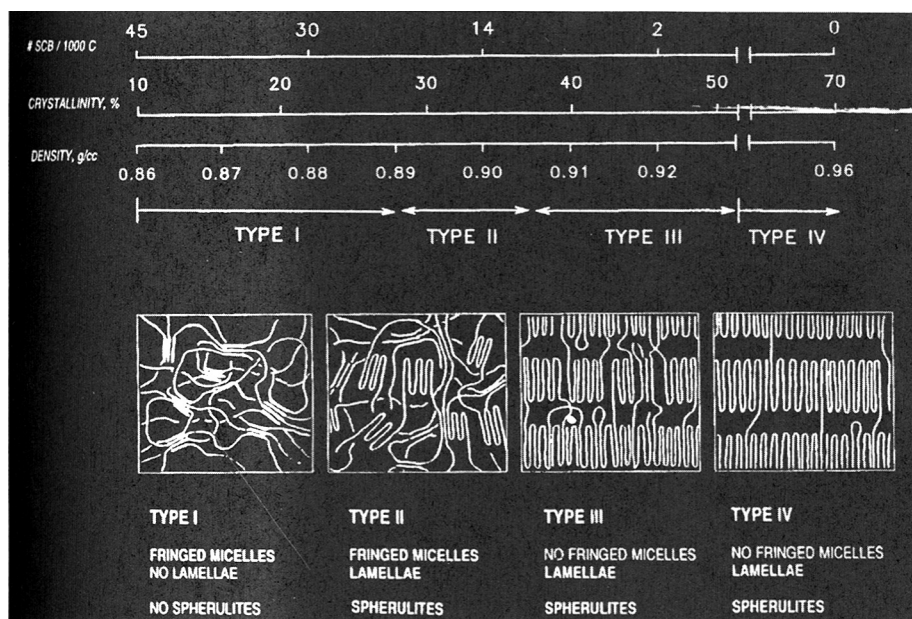


Figure 8 Schematic illustration of the solid-state morphologies of four types of poly (ethylene-co-octene) copolymers. #SCB/1000 C is defined as the number of side chain branches per 1000 backbone carbon atoms. (From Ref. 50.)

or short bundled structures (Figure 8). Higher-order morphologies such as lamellae or spherulites are not observed. Therefore, the physical properties of semicrystalline OCPs fall in between those of polyethylene and amorphous ethylene/propylene rubber.

Polyethylene is a rigid, high-modulus solid at room temperature. Amorphous ethylene/propylene rubber is a relatively soft material under ambient conditions which cold-flows and exhibits a tacky feel. The degree of tack is inversely proportional to molecular weight and can be reduced by the incorporation of long-chain branching. Solid bales of this type of rubber are easily compressed and further densify during storage. Semicrystalline OCPs hold their shape during storage but are slightly tacky to the touch. Higher-compression pressures, longer compression times, and higher finishing temperatures are required to successfully produce dense bales. Typical physical properties of ethylene-propylene copolymers are summarized in Table 1.

5.2 Effect of Copolymer Composition on Rheological Properties in Solution

5.2.1 Low-Temperature Rheology

Rubin et al. [51–57] and others [58] measured the intrinsic viscosity $[\eta]$ of ethylene-propylene copolymers as a function of temperature in various solvents (Figure 9). Intrinsic viscosity, a measure of polymer coil size in dilute solution, is fairly insensi-

Table 1 Typical Physical Properties of Ethylene-Propylene Copolymers

Property	Typical value
Density, kg/m ³	860
Heat capacity, cal/g °C	0.52
Thermal conductivity, cal/cm s °C	8.5×10^{-4}
Thermal diffusivity, cm ² /s	9.2×10^{-4}
Thermal coefficient of linear expansion, /°C	2.2×10^{-4}

Source: Ref. 36.

tive to temperature for noncrystalline OCPs. Semicrystalline copolymers undergo a precipitous drop in $[\eta]$ as temperature drops below about 10°C. In this region, the polymer begins to crystallize, forming intermolecular associations that effectively cause the molecule to shrink in on itself yet remain sufficiently solvated to remain suspended in oil solution.

The viscosity of a dilute polymer solution often follows the Huggins equation [64]:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \quad (10.1)$$

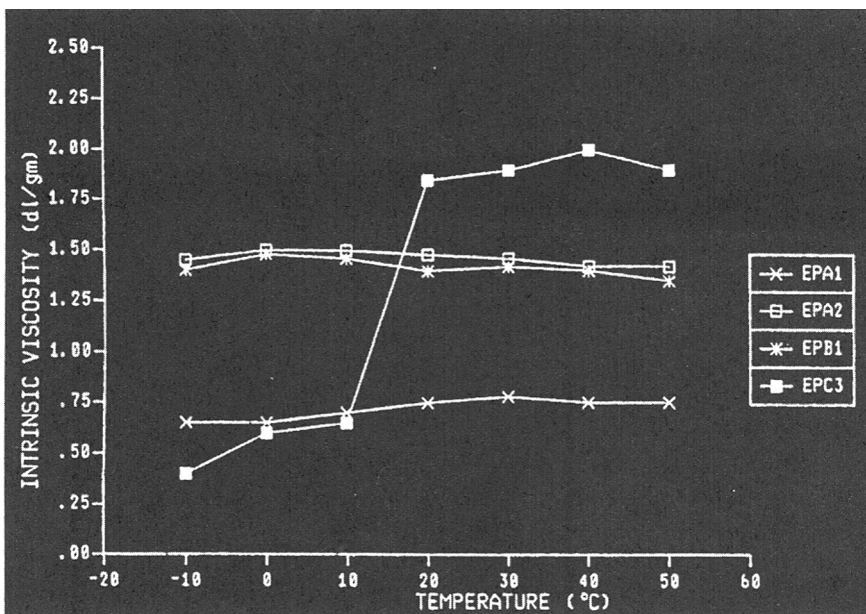


Figure 9 Intrinsic viscosities of EP copolymers in SNO-100 base oil at various temperatures. EPC3, EPB1, EPA2 and EPA1 have 73, 61, 50, and 50 weight % ethylene, respectively. Differences in intrinsic viscosity above 20°C are attributable to differences in molecular weight. (From Ref. 56.)

where

- c = polymer concentration (g/dL).
- η_{sp} = specific viscosity $(\eta - \eta_o) / \eta_o$.
- η = solution viscosity.
- η_o = solvent viscosity.
- k' is a constant.

Thus, for a specific lubricant composition, c and η_o are fixed, and the temperature dependence of the solution viscosity is directly related to that of the intrinsic viscosity.

Low-temperature viscosity is an important rheological feature of automotive lubricants. For the vehicle to start in cold weather, the lubricant viscosity in the bearings should be below a critical value as determined by low-temperature engine startability experiments [7] and defined within SAE J300 [60] for all “W” grades. The cold cranking simulator test, CCS, ASTM D5293, is a high-shear-rate rheometer operating at fixed subambient temperatures, designed to simulate oil flow in automotive bearings during start-up. After the engine starts, the lubricant must also be able to freely flow into the oil pump and throughout the internal oil distribution channels of the engine. This is the other half of the low-temperature viscosity specification for motor oils [60]. The minirotary viscometer, MRV, ASTM D4684, is a low-shear-rate rheometer designed to simulate pumpability characteristics of a multi-grade oil in a vehicle that was sitting idle for about two days in cold weather. SAE J300 also contains upper viscosity limits for MRV viscosity and yield stress for all “W” grades.

Thus, the mechanism of intermolecular crystallization, which leads to molecular size contraction in solution, affords high-ethylene OCP viscosity modifiers the opportunity to contribute less to viscosity at low temperatures than noncrystalline or amorphous copolymers of similar molecular weight. For this reason, the class of ethylene-propylene copolymers having ethylene content greater than about 60 weight % is often called low-temperature OCPs, or LTOCPs. A rheological comparison of two LTOCPs and one conventional OCP viscosity modifier in several SAE 5W-30 oil formulations may be found in [Figures 10](#) and [11](#). These data illustrate the low-temperature rheological benefits of LTOCPs.

A number of workers have cautioned, however, that the long ethylene sequences of LTOCPs are similar in structure to paraffin wax and can interact with waxy base oil components at low temperatures. In many cases, they require specially designed pour point depressants to function properly in certain base stocks. Thus, LTOCP viscosity modifiers have been implicated in problems such as MRV failures in comingled fresh oils [61] and used passenger car lubricants [62–63].

5.2.2 High-Temperature Rheology

Copolymer composition has less influence on high-temperature rheological behavior than it has at low temperatures, partly because lightly crystalline OCPs have melting points well below 100°C [53]. Since both high-temperature kinematic viscosity (KV) and high-temperature, high-shear-rate viscosity (HTHS) are used to classify multi-grade engine oils [60], it is important to understand how copolymer composition and molecular weight influence these key parameters.

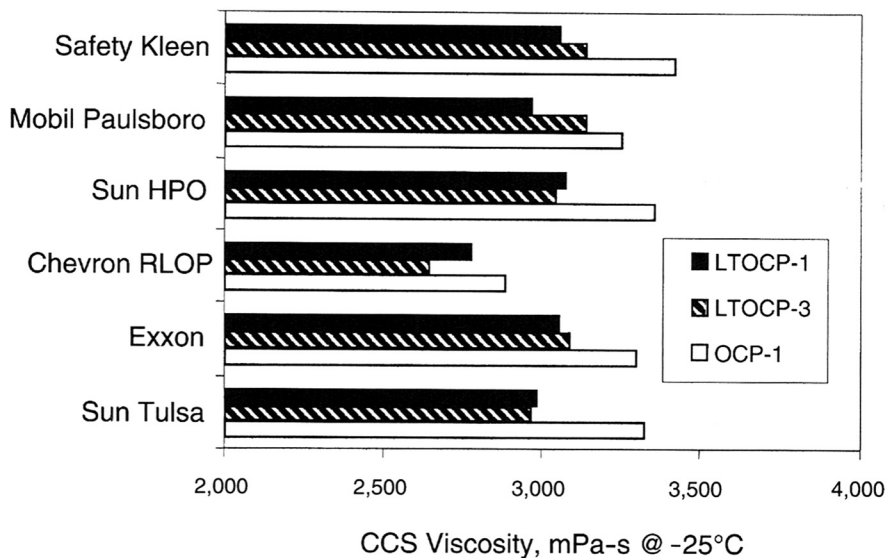


Figure 10 Cold cranking simulator viscosity for six SAE 5W-30 lubricant formulations, each blended with one of three viscosity modifiers: LTOCP-1, LTOCP-3, or OCP-1. Within each base oil type, the ratio of high- and low-viscosity base oil was kept constant.

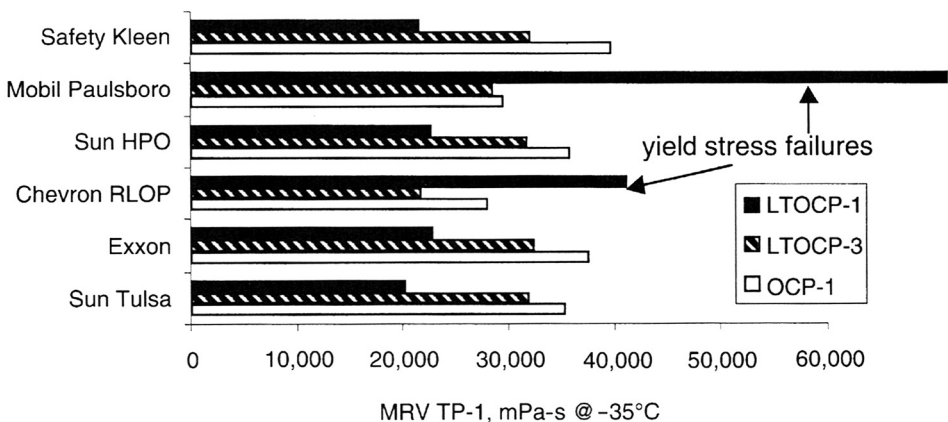


Figure 11 Minirotary viscosity results for six SAE 5W-30 lubricant formulations, each blended with one of three viscosity modifiers: LTOCP-1, LTOCP-3, or OCP-1. Within each base oil type, the ratio of high- and low-viscosity base oil and the type and concentration of pour point depressant were held constant.

Kinematic Viscosity

For both economic and performance reasons, it is desirable to limit the amount of polymer needed to achieve a given set of rheological targets. Therefore, it is important to quantify the effects of molecular-weight, molecular-weight distribution, and branching on thickening efficiency. Thickening efficiency has been defined in many ways, but the most common definitions are (1) the amount of polymer necessary

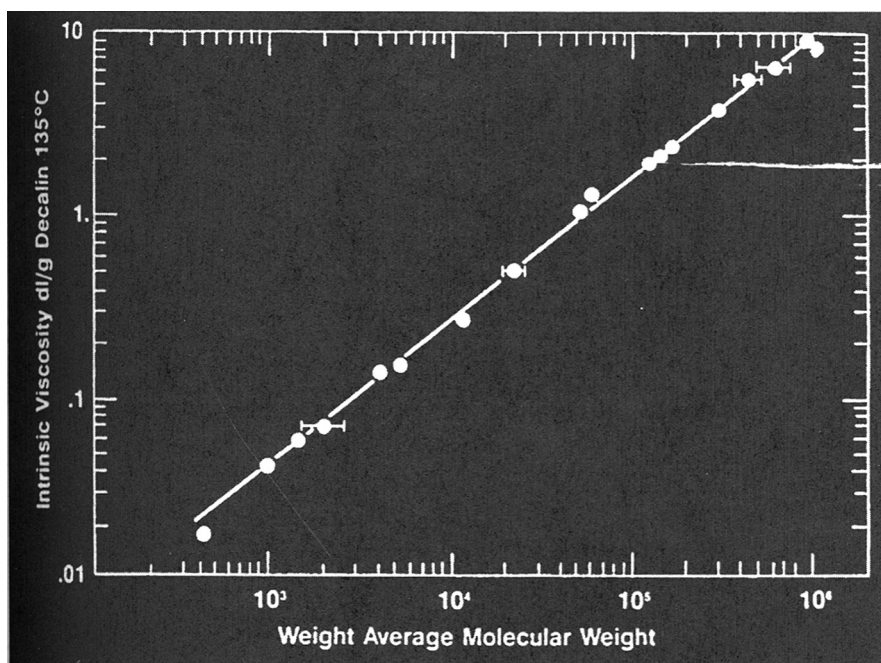


Figure 12 Intrinsic viscosity as a function of weight average molecular weight for ethylene-propylene copolymers of narrow polydispersity ($M_w / M_n \sim 2$). (From Ref. 1.)

to increase the KV of a reference oil to a certain value or (2) the KV or specific viscosity (see Section 6.2.1) of a given polymer concentration in a reference oil. For polymers of equal molecular weight, thickening efficiency increases with ethylene content and is highest for copolymers with narrow molecular-weight distributions [1,2]. A plot of intrinsic viscosity versus weight average molecular weight (Figure 12) demonstrates the familiar Mark-Houwink power law relationship:

$$[\eta] = K' M^a \quad (10.2)$$

Assuming a single value for the power law constant $a = 0.74$, Crespi and co-workers [5] published a table of K' values as a function of ethylene content which is reproduced in Table 2. This clearly shows that thickening efficiency can be improved by increasing ethylene concentration.

This is further illustrated by plotting data from Kapuscinski et al. [54] in Figure 13. The 80 mole % ethylene copolymer requires less polymer to achieve a target viscosity than a 60 mole % copolymer; therefore, the former has a higher thickening efficiency than the latter.

Long-chain branching has a directionally detrimental effect on thickening efficiency for polymers of equal molecular weight. This is not surprising, since the average chain end-to-end distance of a random coil in solution is controlled, in large part, by the length of the main chain. Branching essentially shortens the chain and lowers its hydrodynamic radius. For example, Table 3 contains thickening efficiency data for two sets of noncrystalline OCP viscosity modifiers, one linear and the other containing 2% branching agent, each set differing only in molecular weight.

Table 2 Mark–Houwink K' Constants for Ethylene-Propylene Copolymers Containing Different Mole Percentages of Ethylene ($a=0.74$)

Mole % ethylene	$K' \times 10^4$	Mole % ethylene	$K' \times 10^4$
5	2.020	55	3.020
10	2.115	60	3.140
15	2.205	65	3.260
20	2.295	70	3.385
25	2.390	75	3.515
30	2.485	80	3.645
35	2.585	85	3.790
40	2.690	90	3.940
45	2.795	95	4.240
50	2.910		

Source: Ref. 5.

High-Temperature, High-Shear-Rate (HTHS) Viscosity

Since concentric journal bearings operate in the hydrodynamic or elasto-hydrodynamic lubrication regimes, oil film thickness is a critical factor influencing wear [64,65]. For this reason, SAE J300 specifies a minimum HTHS viscosity for each viscosity grade [60]. HTHS viscosity is measured at very high shear rates and temperatures (10^6 s^{-1} and 150°C , respectively), which is similar to the flow environment in an operating crankshaft bearing at steady state. At these rates of deformation, most high-molecular-weight polymers will align with the flow field [66], and a temporary reduction in viscosity is measured. The difference between low-and

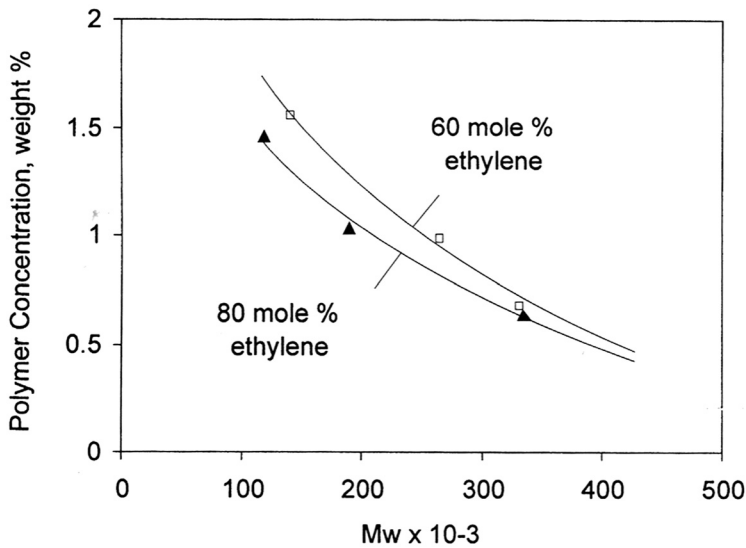


Figure 13 Polymer concentration needed to raise the kinematic viscosity of a 130N base oil to 11.5 cSt. (Data from Ref. 54.)

Table 3 Thickening Efficiency* of Linear and Branched OCP Viscosity Modifiers

Mw	Linear	Branched
230,000	13.50	12.03
180,000	11.17	10.87

*Thickening efficiency is defined as the kinematic viscosity (at 100°C) of a 1.0 weight % polymer solution in 6.05 cSt mineral oil.

Table 4 Rheological Comparison of Lubricants Containing OCP Viscosity Modifiers Differing in Molecular Weight

Viscosity modifier	Wt. average molecular weight	PSSI	Capillary viscosity cP @ 150°C	HTHS cP @ 150°C	% TVL
OCP 1	160,000	45	5.33	3.43	36
OCP 2	80,000	30	5.33	3.77	29
OCP 3	50,000	22	5.33	3.88	27

Source: Ref. 1.

high-shear-rate viscosity at 150°C is termed “temporary viscosity loss” (TVL) or “percent temporary viscosity loss” (relative to the low-shear-rate kinematic viscosity). As is true for most polymers [66], TVL is proportional to molecular weight [1], as shown in Table 4. For polymers of equal weight average molecular weight, those with narrow molecular-weight distributions undergo less temporary viscosity loss than those with broad M_w / M_n values [1].

HTHS viscosity can be adjusted by increasing the viscosity of the base oil or by increasing the viscosity modifier concentration, as shown in Figure 14. Since the formulation also has to meet kinematic viscosity and cold cranking simulator viscosity limits, there is often only limited flexibility to adjust HTHS viscosity within the bounds of a given set of base oils and additives.

Permanent Shear Stability

The tendency of an OCP molecule to undergo chain scission when subjected to mechanical forces is dictated by its molecular weight, molecular-weight distribution, ethylene content, and degree of long-chain branching. Mechanical forces that break polymer chains into lower-molecular-weight fragments are elongational in nature, causing the molecule to stretch until it can no longer bear the load. This loss in polymer chain length leads to a permanent degradation of lubricant viscosity at all temperatures. In contrast to temporary shear loss, permanent viscosity loss (PVL) represents an irreversible degradation of the lubricant and must be taken into account when designing an engine oil for commercial use.

Permanent viscosity loss, PVL, is similar to TVL, except that the viscosity loss is measured by kinematic viscosity before and after shear. Permanent shear stability is more commonly defined by the permanent shear stability index, PSSI or simply SSI, according to ASTM D6022:

$$\text{PSSI} = \text{SSI} = 100 \times (V_o - V_s) / (V_o - V_b) \tag{10.3}$$

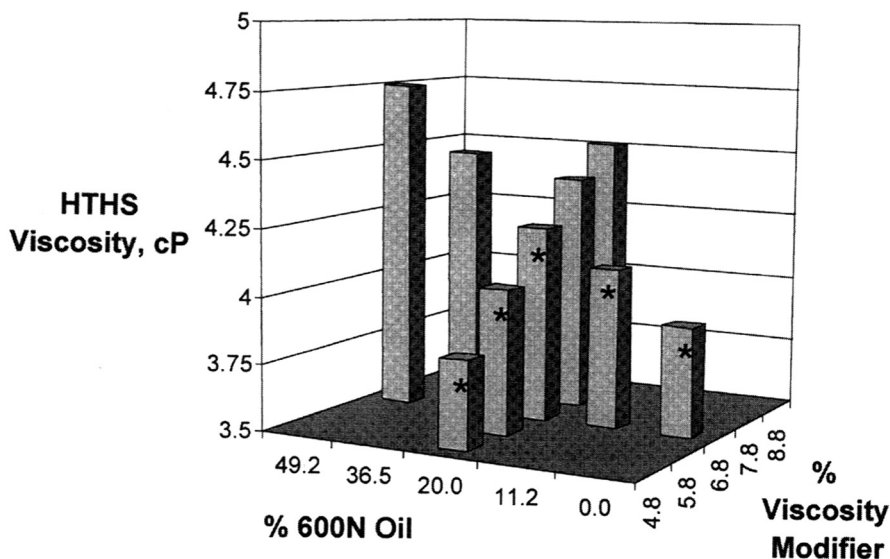


Figure 14 The effects of base oil composition and viscosity modifier concentration on high-temperature, high-shear-rate viscosity. SAE 15W-40 engine oil consisting of European API Group 1 base oils (150N + 600N), an ACEA A3-98 /B3-98 quality performance additive, an oil-diluted amorphous OCP VM, and a pour point depressant. Bars marked with an asterisk comply with ASTM D445 and D5293 limits for SAE 15W-40 oils.

where

V_o = viscosity of unsheared oil.

V_s = viscosity of sheared oil.

V_b = viscosity of the base fluid (without polymer).

SSI represents the fraction of viscosity contributed by the viscosity modifier that is lost during shear. SSI is proportional to \log_{10} molecular weight (M_w), as shown in Figure 15. Commercial OCP viscosity modifiers have SSI values in the 23–55 range.

Although ASTM D6022 provides a definition for SSI, it is important to recognize that the only component responsible for viscosity loss during shear is the high-molecular-weight polymer. If the additive for which SSI is to be calculated happens to be a concentrated polymer solution in oil, according to the strict definition of ASTM D6022, the composition of the “base fluid” does not include the VM diluent oil. Since the diluent oil viscosity is usually lower than the base blend viscosity for most viscosity grades, V_b is higher than it would be if the VM diluent oil viscosity were factored into V_b . For example, take an SAE 15W-40 engine oil formulated with a liquid OCP concentrate containing 10 weight % polymer in a 5.1 cSt mineral oil. V_o and V_s are 15.2 and 12.8 cSt, respectively. The base blend viscosity (when the VM component is a liquid) is 9.4 cSt. When the VM component is defined as the solid polymer, V_b is 9.15 cSt. Calculated shear stability index values are 41.4 and 39.7, respectively. Thus, the numerical value of SSI is dependent on the definition of the polymeric additive in question.

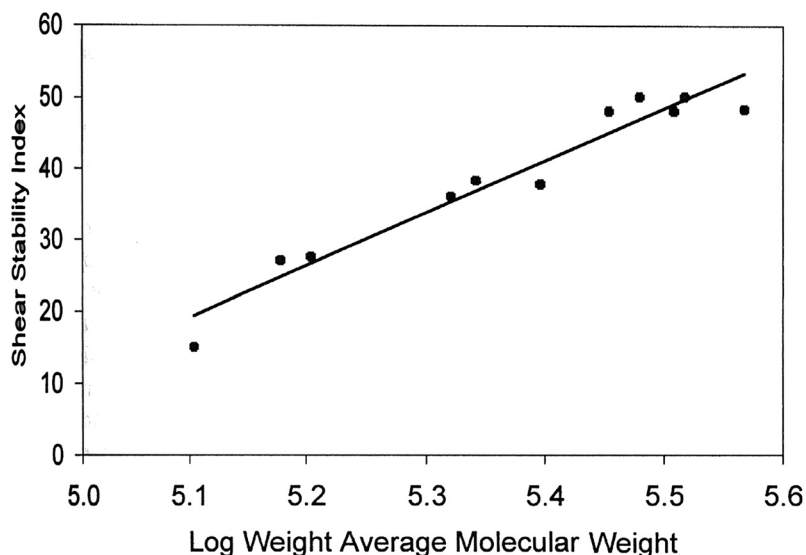


Figure 15 Relationship between weight average molecular weight and SSI (ASTM D3945) for a series of OCP viscosity modifiers.

The concept of “stay-in-grade” is generally used to refer to lubricating oil, when tested in vehicles or laboratory shearing devices, which maintains its kinematic viscosity within the limits of its original SAE viscosity grade. The problem with viscosity measurements of engine drain oils is that many factors other than permanent polymer shear influence viscosity—such as fuel dilution, oxidation, and soot accumulation. Therefore, it is customary to measure PVL after shear in a laboratory rig, the most common being the Kurt Orbahn test, ASTM D6278. Several reviews of methods for determining the shear stability of polymer-containing lubricating oils have been published [67–69].

Selby devised a pictorial scheme for mapping the effects of shear rate and PVL on high-temperature viscosity, the viscosity loss trapezoid, VLT [70], shown in Figure 16. The corners of the “trapezoid” are defined by viscosity data, and the points are connected by straight lines. Note that the straight lines do *not* imply a linear relationship between viscosity and shear rate. The VLT is a convenient graphical representation of the temporary and permanent shear loss characteristics of polymer-containing oils. Molecular-weight degradation causes a permanent loss in both kinematic viscosity and HTHS, but the magnitude of the former is always larger than the latter. The shape of the VLT is characteristic of polymer chemistry and molecular weight.

It is experimentally observed [71] that the Kurt Orbahn shear test breaks molecules above a threshold molecular size; molecules smaller than the threshold value are resistant to degradation. Selby [70] uses this observation to derive certain qualitative conclusions of the polymer molecular-weight distribution from the shape of the VLT.

5.3 Effect of Diene on Thermal/Oxidative Stability

Little solid scientific data have been published in the literature to compare the relative thermal and oxidative stability of oil solutions containing ethylene-propylene

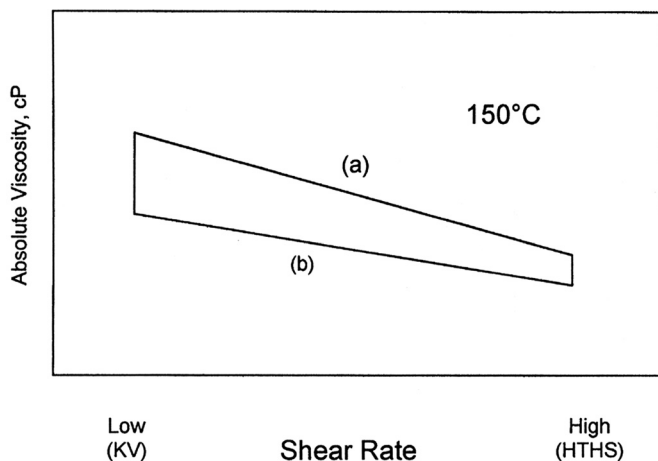


Figure 16 Viscosity loss trapezoid, per Selby (from Ref. 70). (a) fresh oil viscosities; (b) oil viscosities after permanent shear.

copolymers versus EPDM terpolymers. Marsden [2] states that “introduction of a monomer . . . can . . . detrimentally affect shear and oxidation stability, dependent on the monomer,” but he offers no data. Others [5,36] cite high-temperature aging experiments on solid rubber specimens which demonstrate that EP copolymers are more stable (in terms of tensile properties) than EPDM terpolymers of similar ethylene-to-propylene ratio. Copolymers containing higher levels of ethylene are claimed to have better thermal/oxidative stability than more propylene-rich copolymers, presumably due to the lower concentration of oxidatively labile tertiary protons contributed by the propylene monomer. High thermal stresses are sufficient to promote hydrogen abstraction by a free-radical mechanism. The relative susceptibility of protons to hydrogen abstraction follows the classical order tertiary > secondary > primary. In the presence of oxygen, peroxy radicals are formed that can accelerate the degradation process.

Despite these suggestions that diene-containing ethylene-propylene copolymers may be less thermally stable than EP copolymers, the author is not aware of any definitive studies that have shown that EPDM viscosity modifiers are more likely to degrade in service than EP copolymers. Indeed, engine oils formulated with both types have been on the market for years.

5.4 Comparative Rheological Performance in Engine Oils

The most influential factors governing the rheological performance of OCPs in engine oils are molecular weight and monomer composition. The effects of molecular weight and molecular-weight distribution are discussed in Section 5.2.3, and the influence of ethylene-to-propylene ratio on low-temperature rheology is covered in Section 5.2.1. This section presents two comparative rheological studies to further illustrate the links between OCP structure and rheological performance.

5.4.1 Comparative Study of OCP Viscosity Modifiers in a Fixed SAE 5W-30 Engine Oil Formulation

There are two ways to compare the relative performance of several viscosity modifiers. One is to choose a fixed engine oil formulation where the base oil composition and additive concentrations are held constant, and the VM level is adjusted to achieve a certain 100°C kinematic viscosity target. The other is to adjust both base oil composition and VM concentration to achieve predetermined kinematic viscosity and cold cranking simulator viscosity targets. Section 5.4.1 offers an example of the first, and Section 5.4.2 illustrates the second approach.

Four OCP viscosity modifiers were blended into an SAE 5W-30 engine oil composition consisting of a 95/5 w/w blend of Canadian 100N/250N mineral base stocks, an ILSAC GF-2 quality performance additive, and a polyalkylmethacrylate pour point depressant. The viscosity modifiers are described in Table 5. OCP1 and OCP2 are high-SSI polymers differing in both E/P ratio and diene content. OCP3 and OCP4 are progressively more shear stable and have essentially 0% crystallinity.

Rheological data are summarized in Table 6. Comparing OCP1 and OCP2, the former is a more efficient thickener because it contains no long-chain branching (no diene monomer) and it has a higher ethylene content (see Figure 13). The latter property also manifests itself in lower cold cranking simulator (CCS) viscosity. The MRV viscosity is also lower for OCP1 relative to the other amorphous OCPs, but this is highly dependent on the particular pour point depressant chosen for this study. The fact that most of the oils displayed yield stress failures at -35°C shows that the PPD was not optimized for this particular set of components.

As SSI decreases from OCP1 to OCP4, the polymer concentration needed to reach a kinematic viscosity target of 10 cSt increases. In other words, polymer thickening efficiency is proportional to shear stability index. Among the noncrystalline OCP's increasing polymer level causes the CCS viscosity to increase. Since all oils were formulated with the same base oil composition, high-temperature, high-shear-rate viscosity (HTHS) is relatively constant, independent of OCP type. OCP4, the lowest molecular-weight polymer, should have the lowest degree of temporary viscosity loss, and it indeed has the highest HTHS viscosity of the group.

5.4.2 Comparative Study of 37 SSI OCP Viscosity Modifiers in an SAE 15W-40 Engine Oil Formulation

In this example, the base oil ratio and polymer concentration were adjusted to achieve the following targets: kinematic viscosity = 15.0 cSt and CCS = 3000 cP at -15°C. The base stocks were API Group I North American mineral oils, the additive

Table 5 Properties of OCP Viscosity Modifiers used in Table 6

Viscosity modifier code	Shear stability index (ASTM D6278)	Copolymer type
OCP1	55	EP, LTOCP
OCP2	50	EPDM, amorphous
OCP3	37	EP, amorphous
OCP4	25	EP, amorphous

Table 6 Rheological Properties of SAE 5W-30 Engine Oils Containing Different OCP Viscosity Modifiers

	OCP1	OCP2	OCP3	OCP4
Polymer content, wt. %	0.58	0.71	0.73	1.05
Kinematic viscosity, cSt 100°C	10.17	10.09	9.99	10.10
Viscosity index	156	160	160	158
CCS viscosity, cP −25°C	3,080	3,280	3,510	3,760
MRV viscosity, cP −30°C	13,900	26,500	26,700	28,100
MRV viscosity, cP −35°C	40,100	yield stress	yield stress	yield stress
HTHS, cP	2.95	2.88	2.96	3.07

Table 7 OCP Viscosity Modifiers Used in Rheological Study in Table 8

Viscosity modifier code	Copolymer type
OCP7	EPDM, amorphous
OCP3	EP, amorphous
OCP8	EPDM, LTOCP
OCP9	EP, LTOCP

package was of API CH-4 quality level, and the pour point depressant was a styrene ester type optimized for these base oils. All viscosity modifiers (see Table 7) were nominally 37 SSI according to ASTM D6278. Rheological results are summarized in Table 8.

OCP 3 is the same polymer as in Table 5. Although OCP 8 and OCP 9 are semicrystalline LTOCPs, they represent different manufacturing technologies, broadly described in Figures 4 and 5, respectively. Incidentally, OCP1 in Table 5 was also manufactured by the tubular reactor technology described in Figure 5.

The rheological data in Table 8 further illustrate several features of LTOCPs mentioned earlier. Their inherently lower CCS viscosity contributions permit the greater use of higher-viscosity base oils, which can be beneficial in meeting volatility requirements. The low-temperature MRV performance of OCP9 was far inferior to that of the other copolymers, indicating that the pour point depressant chosen for this particular study was not optimized for OCP9 in these base stocks.

Another polyalkymethacrylate pour point depressant was found to bring the MRV viscosity of the OCP9 formulation down to 7,900 and 18,000 cP at −20 and −25°C, respectively. More is said about interaction with pour point depressants in Section 5.7.

Again, the higher thickening efficiency of E/P copolymers versus EPDMs of similar molecular weight (shear stability) is clearly demonstrated in Table 8. Another feature worth noting is that increasing base oil viscosity can nudge HTHS viscosity upward (compare OCP7 with OCP8 or OCP3 with OCP9).

Table 8 Rheological Properties of SAE 15W-40 Engine Oils Containing Different OCP Viscosity Modifiers

	OCP7	OCP3	OCP8	OCP9
Polymer content, wt. %	0.95	0.85	0.85	0.64
150N base oil percentage	76	76	70	70
600N base oil percentage	24	24	30	30
Kinematic viscosity, cSt 100°C	15.04	14.97	15.25	15.12
Viscosity index	141	140	140	135
CCS viscosity, cP -15°C	3,080	3,040	3,070	3,010
MRV viscosity, cP -20°C	10,000	9,900	8,800	solid
MRV viscosity, cP -25°C	20,500	18,600	18,300	solid
HTHS, cP	4.17	4.38	4.25	4.42

5.5 Interaction with Pour Point Depressants

Although base oil and VM play a role in determining low-temperature oil pumpability, the pour point depressant provides the primary control in this area. SAE J300 [65] specifies the MRV test (ASTM D 4684) as the sole guardian of pumpability protection, although it acknowledges that other tests may also be useful in the development of lubricants from new components. The Scanning Brookfield test (ASTM D5133) and Pour Point (ASTM D 97), although not required within SAE J300, are often contained in other standards established by original equipment manufacturers, oil marketers, and governmental agencies and, therefore, must also be considered in the development of modern engine oils.

Advances in base oil technology have led, in recent years, to a wide range of mineral and synthetic lubricant base stocks [72], classified as API Groups I, II, III, IV, and V stocks. The API system classifies oils according to viscosity index (VI), saturates content, and sulfur level. Group I mineral oils are defined as having less than 90% saturates, VI greater than 80 and more than 0.03% sulfur. Groups II and III oils have less than 0.03% sulfur and greater than 90% saturates, but they differ mainly in VI. Group II oils have VI greater than 80, whereas Group III stocks have VI values in excess of 120.

Formulating these conventional and highly refined oils to meet all the rheological requirements of SAE J300 is not always straightforward. An important aspect of base oil technology that is not embodied within the API Group numbering scheme is the type of dewaxing process or processes employed. It is well known [73–79] that the low-temperature oil pumpability performance of engine oils is often impeded by the nucleation and growth of wax crystals, which can coalesce and restrict the flow of oil at low temperatures. The type and amount of wax that forms dictates the type and concentration of pour point depressant that will be effective in keeping wax crystals small so they do not form network structures and lead to high viscosity and yield stress. Both the feedstocks and dewaxing steps used in the manufacture of a given base oil determine wax composition and, in turn, PPD response.

Table 9 Base Oils Used in Low-Temperature Viscosity Modifier/Pour Point Depressant Interaction Study

Base oil code (API Group)	Saturates, wt. %	Kinematic viscosity cSt @ 100°C	Sulfur wt. %	Viscosity index	CCS viscosity, cP @ -25°C
B1-L(I)	73.6	3.88	0.276	104	1170
B1-M(I)	71.8	5.15	0.553	102	4060
B1-H(I)	61.8	12.10	0.381	97	—
B2-L(I)	75.2	4.18	0.193	105	1510
B2-M(I)	75.0	4.91	0.544	106	3060
B2-H(I)	72.3	12.73	0.412	99	—
B3-L(II)	100	4.20	0.006	100	1570
B3-M(II)	100	5.49	0.011	117	2430
B3-H(II)	100	10.72	0.016	98	—
B4-L(III)	100	4.50	0.007	123	1120
B4-H(III)	100	6.49	0.006	131	2710

Certain types of viscosity modifiers can interact with base oils and pour point depressants at low temperatures and can lead to excessively high MRV viscosities in some situations (see, for example, OCP9 in Table 8). Formulating with amorphous OCPs has not, in the author's experience, posed many difficulties. Conversely, LTOCPs possess longer ethylene sequences, which have the potential to interact with wax crystals at low temperatures. Several reports in the literature [61,71] suggest that high-ethylene OCPs can, under certain circumstances, interact negatively on MRV viscosity and yield stress and may be more sensitive to the type of pour point depressants that will be effective in some formulating systems.

A previously unpublished study of low-temperature interactions among base oils, OCP viscosity modifiers, and pour point depressants was carried out in the author's laboratory using components listed in Tables 9–11.

Fully formulated SAE 5W-30 and 15W-40 engine oils were blended using performance additive packages DI-1 (at 11 wt. %) and DI-2 (at 13 wt. %), API SJ quality, and CH-4 quality, respectively, and all combinations of base oil, VM, and PPD.

Figures 17 to 20 summarize VM/PPD effects on MRV viscosity for each base oil type. In these graphs, the letter Y adjacent to a vertical bar denotes a yield stress failure. For the API Group I base oil B1 (SAE 5W-30, Figure 17), only PPD-3 is effective with all three viscosity modifiers. Both VM-1 and VM-3 suffer yield stress failures with at least one PPD. In the 15W-40 formulation, VM-3 exhibits yield stress

Table 10 Viscosity Modifiers Used in Low-Temperature Viscosity Modifier/Pour Point Depressant Interaction Study

VM code	OCP type	SSI (ASTM D6278)
VM-1	amorphous	37
VM-2	LTOCP	35
VM-3	LTOCP	37

Table 11 Pour Point Depressants Used in Low-Temperature Viscosity Modifier/Pour Point Depressant Interaction Study

Pour point depressant code	Chemistry
PPD-1	Poly(styrene-maleate ester)
PPD-2	Poly(alkylmethacrylate)
PPD-3	Poly(styrene-maleate ester)
PPD-4	Poly(alkylmethacrylate)

behavior with all four PPDs, even in one case in which the MRV viscosity is quite low (PPD-1). In the author’s experience, it is quite unusual to observe yield stress failures in the MRV test when viscosity is below about 40,000 cP.

The other API Group I blended oils, B2 (Figure 18), respond to PPDs in a similar manner to B1, but only in the SAE 5W-30 formulation. In the 15W-40 case, VM-3 is the only VM to experience yield stress failure, but only in the presence of PPD-2; all other combinations demonstrate acceptable pumpability performance.

Figure 19 describes the MRV map of B3, the API Group II oil. Overall low-temperature viscosities are quite low for all VM/PPD combinations, although VM-3 again experiences one yield stress failure in each viscosity grade. VM-1 fails the yield stress criterion once.

Finally, the API Group III SAE 5W-30 formulation (Figure 20) was the most difficult to pour depress. All four oils blended with VM-3 were yield stress failures, and each of the other two VMs showed significant yield stresses for one PPD each.

In summary, the number of MRV failures due to yield stress may be found in Table 12. Clearly, one of the LTOCP viscosity modifiers, VM-3, is substantially more sensitive to pour point depressants than the other two polymers. It is especially incompatible with PPD-2. The other LTOCP in this study, VM-2, and the amorphous VM-1 were found to be far more tolerant of PPD type. Similar to the discussion in Section 5.4.2, one of the major differences between VM-3 and VM-2 is that they were manufactured by different technologies, broadly described in Figures 5 and 4, respectively.

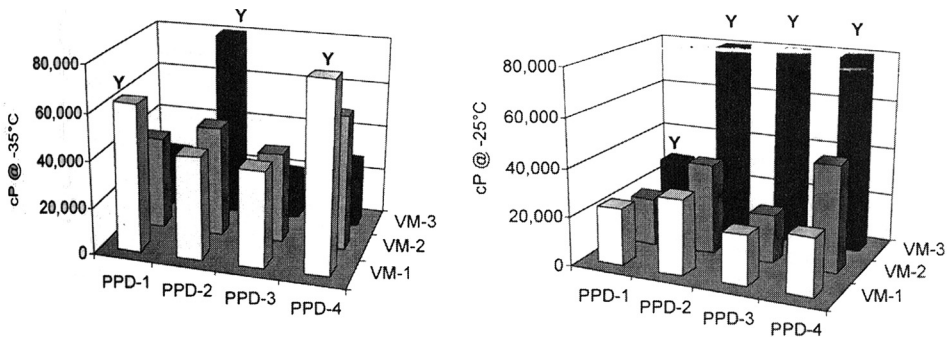


Figure 17 Rheological results for oil B1. SAE 5W-30 (left) and SAE 15W-40 (right).

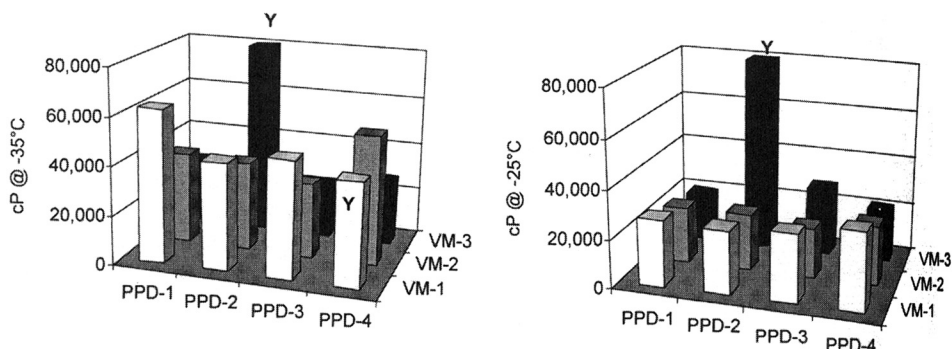


Figure 18 Rheological results for oil B2. SAE 5W-30 (left) and SAE 15W-40 (right).

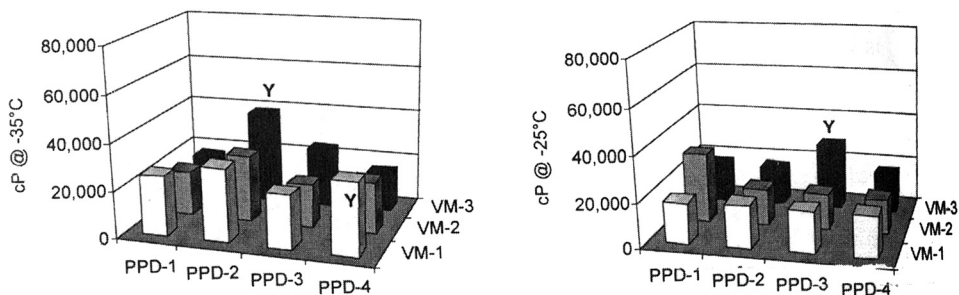


Figure 19 Rheological results for oil B3. SAE 5W-30 (left) and SAE 15W-40 (right).

5.6 Field Performance Data

Multigrade lubricants containing ethylene/propylene viscosity modifiers have been tested in passenger car and heavy-duty truck engines for over three decades, but very few studies devoted to VM effects on engine cleanliness and/or wear have been published. It is generally believed that adding a polymer to the engine lubricant will have a detrimental effect on engine varnish, sludge, and piston ring-pack deposits [1,2], but the performance additive can be formulated to compensate for these effects. Kleiser and co-workers [80] ran a taxicab fleet test designed to compare the performance of a nonfunctionalized OCP viscosity modifier with a highly dispersant-functionalized OCP (HDOCP) as well as to test other oil formulation effects. They were surprised to find that an SAE 5W-30 oil containing a higher concentration of non-dispersant OCP showed statistically better engine deposit control when compared with a similar SAE 15W-40 oil with lower polymer content. They also observed significant improvements in sludge and varnish ratings attributed to the use of HDOCP. Others have also reported that DOCPs can be beneficial in preventing buildup of deposits in laboratory engines such as the Sequence VE [81], VD [1], and Caterpillar 1H2/1G2 [1] tests. These authors found that engine oils containing certain dispersant-functionalized OCPs need less ashless dispersant to achieve an acceptable level of engine cleanliness than nonfunctionalized OCPs. The actual level

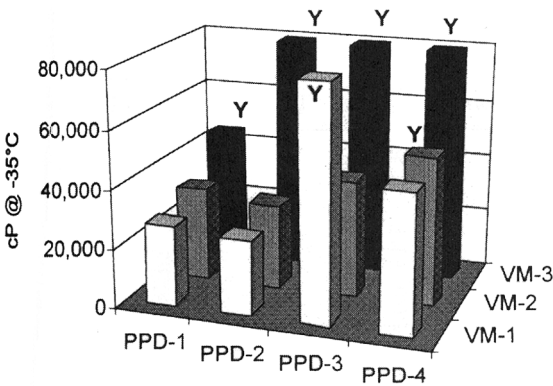


Figure 20 Rheological results for oil B4, SAE 5W-30.

of deposit prevention is highly influenced by the functionalization chemistry as well as the number of substituents per 1000 backbone carbon atoms, as shown in [Table 13](#).

6 MANUFACTURERS, MARKETERS, AND OTHER ISSUES

6.1 EP/EPDM Manufacturers

Ethylene-propylene copolymers and EPDM terpolymers are manufactured by a number of companies worldwide. [Table 14](#) lists those companies with production capacity greater than 30,000 MT/year (65 million pounds per annum). Not all are necessarily supplying rubber into the viscosity modifier market. The vast majority of the capacity goes into other applications such as automotive (sealing systems, radiator hoses, injection molded parts), construction (window gaskets, roofing/sheeting, cable insulation, cable filler), and plastics modification.

Various grades are often classified by melt viscosity, ethylene-to-propylene ratio, diene type and content, physical form, and filler type and level (carbon black, pigments, or extender oils). Melt viscosity is measured by two main techniques, Mooney viscosity (ASTM D1646 or ISO 289) or melt index (ASTM D1238 or ISO 1133–1991, also called melt-mass flow rate). Mooney viscosity is proportional to molecular weight, whereas melt index is inversely proportional to molecular weight.

Table 12 Number of MRV Failures Due to Yield Stress in Low-Temperature Viscosity Modifier/Pour Point Depressant Interaction Study

VM	PPD-1	PPD-2	PPD-3	PPD-4	Total
VM-1	1		1	3	5
VM-2				1	1
VM-3	2	6	3	2	13
Total	3	6	4	6	19

Table 13 120-h Caterpillar 1H2 Piston Deposit Ratings of SAE 10W-40 Oils Formulated with N-Vinyl Pyrrolidone Grafted OCPs

Sample	Nitrogen, wt. %	TGF	WTD
OCP	0	—	>800
MFOCP 5	0.3	46	244
MFOCP 6	0.5	39	173
MFOCP 7	0.7	47	149
MFOCP 6*	0.26	28	156
MFOCP 2*	0.28	11	139

*OCP grafted with maleic anhydride and subsequently reacted with amines.

Source: Ref. 1.

6.2 OCP VM Marketers

Companies that market ethylene/propylene copolymers and terpolymers into the viscosity modifier market are listed in Table 15. A wide variety of products, varying in shear stability and level of crystallinity, are available in both solid and liquid forms. Functionalized polymers, which provide added dispersancy and/or antioxidant, are available from several suppliers. The reader is advised to update this information periodically, since each company's product lines change over time.

Mergers and acquisitions have also contributed to significant flux in the OCP market. For example, the Paratone® product line was originally marketed by the Paramins Division of Exxon Chemical Company. Then Exxon and Shell combined their lubricant additives businesses to form Infineum in 1998; the Paratone business was sold to Oronite, the lubricant additives division of Chevron Chemical Company. Ethyl's purchase of Amoco and Texaco OCP product technology in the 1990s resulted in rebranding of Texaco's TLA-XXXX products to Ethyl's Hitec® product line. Dupont originally marketed EPDM—manufactured at its Freeport, TX, facility—into the viscosity modifier market under the Ortholeum® trademark until it was sold to Octel in 1995. Thereafter, DuPont adopted the NDR brand name, DuPont and Dow Chemical Company formed a 50/50 Joint Venture in 1995, merging their elastomers businesses. Shortly following the successful start-up of their metallocene plant in Plaquemine, LA, two years later, the Freeport facility was closed. The DuPont Dow Elastomers EPDM product line currently is marketed under the Nordel® IP tradename. Although primarily a poly(alkylmethacrylate) company, Rohm GmbH of Darmstadt, Germany, developed several OCP-based viscosity modifiers under the Viscoplex® tradename, currently owned and marketed by RohMax Additives, a Degussa company.

6.3 Read Across Guidelines

Various lubrication industry associations have published highly detailed guidelines [83–85] for defining conditions under which certain additive and base oil changes to a fully or partially qualified engine oil formulation may be permitted without requiring complete engine testing data to support the changes. The purpose of these standards is to minimize test costs while ensuring that commercial engine oils meet

Table 14 Manufacturers with Production Capacity Greater Than 30,000 MT/Y

Company	Manufacturing location	Capacity (metric ton/year)	Technology	Tradename	Comments
Uniroyal Chemical Co., div. of Crompton Corp.	Geismar, LA	91,000	Ziegler–Natta, solution	Royalene	EP and EPDM
DuPont Dow Elastomers	Plaquemine, LA	90,000	Metallocene, solution	Nordel IP	EPDM
Bayer	Orange, TX	52,000	Ziegler–Natta, solution	Buna EP T	EP and EPDM
Bayer	Marl, Germany	50,000	Ziegler–Natta, slurry process	Buna EP G	EP and EPDM
Mitsui	Chiba, Japan	60,000	Ziegler–Natta, solution	Mitsui EPT	EP and EPDM
DSM Elastomers	Addis, LA; Geleen, The Netherlands; Triunfo, Brazil; Chiba, Japan	216,000	Ziegler–Natta, solution	Keltan	EP and EPDM
ExxonMobil Chemical	Baton Rouge, LA; Notre Dame de Gravenchon, France; Kumbo Polychem, South Korea (JV)	170,000	Ziegler–Natta, solution	Vistalon	EP and EPDM
Enichem	Ferrara, Italy	85,000	Ziegler–Natta, slurry process	Dutral	EP and EPDM
Japan Synthetic Rubber	Yokkaichi and Kashima, Japan	65,000	Ziegler–Natta, solution	Esprene	EPDM
Union Carbide	Seadrift, TX	90,000	Gas-phase process	ElastoFlo	EPDM

Source: Ref. 82.

Table 15 Marketers of Ethylene/Propylene Copolymers and EPDM Terpolymers as Engine Lubricating Oil Viscosity Modifiers

Company	Head quarters	Tradename	Product classes*	Product form
Lubrizol	Wickliffe, OH	Lubrizol 7000 series	NDOCP	Bales and liquid concentrates
Infineum	Linden, NJ	Infineum V8000 series	NDOCP	Pellets and liquid concentrates
DuPont Dow Elastomers	Wilmington, DE	Nordel IP	NDOCP	Bales and pellets
Ethyl	Richmond, VA	Hitec 5700 series	NDOCP, DOCP, DAOCP	Liquid concentrates
Oronite (Chevron)	Richmond, CA	Paratone	NDOCP, DOCP	Pellet, bales, and liquid concentrates
RohMax (Degussa AG)	Darmstadt, Germany	Viscoplex	NDOCP, mixed PMA/OCF	Liquid concentrates

*NDOCP = nonfunctionalized OCP, DOCP = dispersant-functionalized OCP, DAOCP = OCP with dispersant and antioxidant functionality; PMA = poly(alkylmethacrylate).

the performance requirements established by industry standards, certification systems, and OEMs. From a viscosity modifier perspective, changes are often driven by one or more of the following needs:

1. To optimize viscometrics within a given viscosity grade
2. To improve the shear stability of the formulation
3. To interchange one polymer for another (cost, security of supply, customer choice)

There are similarities and differences among codes of practice adopted by the American Chemistry Council (ACC) and the two European agencies, ATC (Technical Committee of Petroleum Additive Manufacturers of Europe) and ATIEL (Technical Association of the European Lubricants Industry). All permit minor changes in VM concentration (no more than 10% relative on a mass basis) to accomplish (1) above. The European codes explicitly allow the interchange of one VM for another (if both are from the same supplier) if the VM supplier deems them to be “equivalent and interchangeable.” VMs from different suppliers, or those from the same supplier that are not judged to be “equivalent,” must undergo a rigorous engine-testing program such as that outlined in [Table 16](#).

The ACC guidelines impose two levels of data needed to support viscosity modifier interchange. Level 1 support is defined as analytical and rheological test data. Level 2 support includes both Level 1 data and full-length valid ASTM engine tests, intended to demonstrate that the proposed VM interchange presents no harm in terms of lubricant performance. Three categories of engine tests can be used to satisfy the ACC Level 2 criterion: (1) statistically designed engine test matrices; (2) complete programs; or (3) partial data sets from the same technology family. This broad definition of additive interchange testing is more open for interpretation than the European guidelines as represented in [Table 16](#). Minor formulation modifications needing only Level 1 data do not permit changes in

Table 16 Engine Test Requirements for Interchanging Viscosity Modifiers Within the ATIEL Code of Practice

Performance category	NDVM to NDVM (2, 4)	DVM to DVM or NDVM to DVM (1, 2, 4)
Gasoline	TU3MH or IIIE M111 or VE M111FE	TU3MH or IIIE M111 or VE M111FE
Light-duty diesel	VWICTD VWDI M111FE	OM602A VWICTD XUD11 VWDI M111FE
Heavy-duty diesel	OM364A Mack T8 (3) OM 441 LA	OM364A OM602A Mack T8 (3) OM 441 LA

Source: Ref. 85.

Notes: 1. Full testing required for any other VMI, including DVM to NDVM.

2. Physical mixes of NDVM and DVM are treated as DVM.

3. Mack T8 test only required in the category with pass limits defined by ACEA.

4. Where alternative tests are listed, e.g., "TU3MH or IIIE," the alternative test cannot be run to document read across if a failing result has already been obtained on the other test.

VM type, defined as polymers of a "specific molecular architecture with a specific shear stability characterized by a specific trade name, stock or code number." When a change in shear stability is required, Level 2 support is sufficient for polymers of the same chemical family (e.g., olefin copolymers) and from the same manufacturer. Otherwise, a full engine testing program is needed. The ACC guidelines also specify that if a DVM is used in a core multigrade formulation, the additional dispersant needed to read across to a monograde or other multigrades with lower VM concentration requires a Sequence VE test and Level 2 support in other tests.

6.4 Safety and Health

Copolymers of ethylene and propylene as well as EPDMs are classified as "non-hazardous" substances by OSHA (1910.1200) and the EEC (European Economic

Table 17 EP/EPDM Grades Indexed by Chemical Abstract Service

EP/EPDM	CAS index
EP	9010-79-1
EPDM (ENB termonomer)	25038-36-2
EPDM (DCPD termonomer)	25034-71-3
EPDM (1,4-hexadiene termonomer)	25038-37-3

Community). They are generally considered not to be acutely toxic, similar to other high-molecular-weight polymers. Material that is heated to the molten state can emit fumes that can be harmful and irritating to the eyes, skin, mucous membranes, and respiratory tract, especially copolymers containing nonconjugated diene termonomers. Proper ventilation and respiratory protection are recommended when handling EP and EPDM copolymers under these conditions. Appropriate personal protective equipment is also advised to guard against thermal burns.

EP/EPDM grades are indexed by the Chemical Abstract Service (CAS) as shown in [Table 17](#).

REFERENCES

1. GT Spiess, JE Johnston, G VerStrate. Ethylene propylene copolymers as lube oil viscosity modifiers. *Addit. Schmierst. Arbeitsfluessigkeiten, Int. Kolloq.*, 5th, WJ Bartz, ed., Tech. Akad. Esslingen, 2:8, 10–11, 1986.
2. K Marsden. Literature review of OCP viscosity modifiers. *Lub Sci* 1(3):265, 1989.
3. G Ver Strate. MJ Struglinski. Polymers as lubricating-oil viscosity modifiers. In DN Schulz and JE Glass, eds. *Polymers as Rheology Modifiers*. Am. Chem. Soc. Symp. Series 462:256, 1991.
4. J Boor, Jr. *Ziegler-Natta Catalysts and Polymerizations*. New York: Academic Press, 1979.
5. G Crespi, A Valvassori, U Flisi. Olefin copolymers. In *Stereo Rubbers*, 1977, pp 365–431.
6. J Brandrup, H Immergut, eds. *Polymer Handbook*, 2nd ed. New York: J Wiley & Sons, 1975, p II–193.
7. Cold starting and pumpability studies in modern engines. ASTM Res. Report RR-D02-1442, 1999.
8. CE Wilkes, CJ Carmen, RA Harrington. Monomer sequence distribution in ethylene-propylene terpolymers measured by ^{13}C nuclear magnetic resonance. *J Poly Sci: Symposium* no. 43, 237, 1973.
9. CJ Carmen, KC Baranwal. Molecular structure of elastomers determined with carbon-13 NMR. *Rubber Chem Tech* 48:705, 1975.
10. CJ Carmen, RA Harrington, CE Wilkes. Monomer sequence distribution in ethylene-propylene rubber measured by ^{13}C NMR. 3. Use of reaction probability model. *Macromolecules* 10(3):536, 1977.
11. JC Randall. *Polymer Sequence Determinations: Carbon-13 NMR Method*. New York: Academic Press, 1977, p 53.
12. CJ Carmen. Carbon-13 NMR high-resolution characterization of elastomer systems. In *Carbon-13 NMR in Polymer Science*. ACS Symposium Ser. 103:97, 1978.
13. GS Kapur et al. Structure-performance relationships of viscosity index improvers: I. Microstructural determination of olefin copolymers by NMR spectroscopy. *Lubrication Sci* 8–1:49, 1995.
14. U.S. Patent 4,666,619 (1987).
15. U.S. Patent 4,156,767 (1979).
16. O Olabisi, M Atiqullah. Group 4 metallocenes: Supported and unsupported. *J.M.S.—Rev Macromol Chem Phys* C37(3):519, 1997.
17. JBP Soares, AE Hamielec. Metallocene/aluminoxane catalysts for olefin polymerization. A review. *Poly Reaction Engr* 3(2): 131, 1995.
18. VK Gupta, S Satish, IS Bhardwaj. Metallocene complexes of Group 4 elements in the polymerization of monoolefins. *J.M.S.—Rev Macromol Chem Phys* C34(3):439, 1994.

19. M Hackmann, B Rieger. Metallocenes: Versatile tools for catalytic polymerization reactions and enantioselective organic transformations. *Cat. Tech* 79, Dec. 1997.
20. JCW Chien, D He. Olefin copolymerization with metallocene catalysts. I. Comparison of catalysts. *J Poly Sci Part A: Poly Chem* 29:1585, 1991.
21. AA Montagna, AH Dekmejian, RM Burkhart. The evolution of single-site catalysts. *Chemtech* 26, Dec. 1997.
22. RH McGirk, MM Hughes, LC Salazar. Evaluation of polyolefin elastomers produced by constrained geometry catalyst chemistry as viscosity modifiers for engine oil. *Soc. Automotive Engr. Tech. Paper ser.* 971, 696, 1997.
23. Synthetic rubber. *Chem Week*, p 15, May 14, 1997.
24. U.S. Patent 5,151,204 (1992).
25. MK Mishar, RG Saxton. Polymer additives for engine oils. *Chemtech* 35, April 1995.
26. U.S. Patent 5,698,500 (1997).
27. Eur. Patent 199453 (1986); U.S. Patents 4,092,255 (1978); 4,699,723 (1987); 4,816,172 (1989); 5,814,586 (1998); 5,874,389 (1999).
28. H Pennewib, C Auschra. The contribution of new dispersant mixed polymers to the economy of engine oils. *Lub Sci* 8(2):179–197, 1996.
29. U.S. Patents 4,089,794 (1978); 4,160,739 (1979); 4,171,273 (1979); 4,219,432 (1980); 4,320,019 (1982); 4,489,194 (1985); 4,749,505 (1988); 5,210,146 (1992); 5,252,238 (1993); 5,290,461 (1994); 5,401,427 (1995); 5,427,702 (1995); 5,534,171 (1996).
30. U.S. Patents 4,743,391 (1988); 4,749,505 (1988); 4,169,063 (1979); 4,132,661 (1979).
31. U.S. Patents 4,517,104 (1985); 4,632,769 (1986); 5,540,851 (1998); 5,811,378 (2000).
32. Eur. Patent 338672 (1989); U.S. Patent 5,075,383 (1991).
33. U.S. Patents 4,500,440 (1985); 5,035,819 (1991); Eur. Patents 470698 (1992); 461774 (1991); U.S. Patents 5,021,177 (1991); 4,790,948 (1988); Eur. Patent 284234 (1988).
34. U.S. Patent 6,117,941 (2000).
35. Synthetic rubber is resilient. *Chem Eng* 105(12):30, 1998.
36. L Corbelli. Ethylene-propylene rubbers. *Dev Rubber Tech* 2:87–129, 1981.
37. ET Italiaander. The gas-phase process—a new era in EPR polymerization and processing technology. *NGK Kautschuk Gummi Kunststoffe* 48:742–748, Oct. 1995.
38. Ethylene-propylene rubber. *Hydrocarbon Processing* p 164, Nov. 1981.
39. EPM/EPDM. *Gosei Gomu* 85:1–9, 1980.
40. C Darribère, FA Streiff, JE Juvet. Static devolatilization plants. *DECHEMA Monographs* 134:689–704, 1998.
41. U.S. Patent 3,726,843 (1973).
42. U.S. Patents 4,874,820 (1989); 4,804,794 (1989); 5,798,420 (1998).
43. L Corbelli, F Milani. Recenti sviluppi nella produzione delle gomme sintetiche etilene-propilene. *L-Industria Delia Gomma* 29(5):28–31, 53–55, 1985.
44. HW Young, SD Brignac. The effect of long chain branching on EPDM properties. *Proc. Special Symp. Advanced Polyolefin Tech., 54th Southwest Reg. Meeting Am. Chem. Soc.* Baton Rouge, LA, 1998.
45. F Garbassi. Long chain branching: An open question for polymer characterization? *Polymer News* 19:340–346, 1994.
46. British Patent 1,372,381 (1974); Canadian Patent 991,792 (1976); U.S. Patents 4,464,493 (1984); 4,749,505 (1988); 5,290,461 (1994); 5,391,617 (1995); 5,401,427 (1995); 5,837,773 (1998).
47. U.S. Patents 3,316,177 (1967); 3,326,804 (1967); 4,743,391 (1988); 5,006,608 (1991).
48. U.S. Patents 4,743,391 (1988); 5,006,608 (1991).
49. S Di Martino, M Kelchtermans. Determination of the composition of ethylene-propylene-rubbers using ¹³C-NMR spectroscopy. *J Appl Poly Sci* 56:1781–1787, 1995.
50. J Minick et al. Crystallization of very low density copolymers of ethylene with α -olefins. *J Appl Poly Sci* 58:1371–1384, 1995.

51. ID Rubin, MM Kapuscinski. Viscosities of ethylene-propylene-diene terpolymer blends in oil. *J Appl Poly Sci* 49:111, 1993.
52. ID Rubin. Polymers as lubricant viscosity modifiers. *Poly. Preprints, Am. Chem. Soc. Div Poly Chem* 32(2):84, 1991.
53. ID Rubin, AJ Stipanovic, A Sen. Effect of OCP structure on viscosity in oil. *Soc. Automotive Engr. Tech. Paper Ser.* 902,092, 1990.
54. MM Kapuscinski, A Sen, ID Rubin. Solution viscosity studies on OCP VI improvers in oils. *Soc. Automotive Engr. Tech. Paper Ser.* 892,152, 1989.
55. MJ Kucks, HD Ou-Yang, ID Rubin. Ethylene-propylene copolymer aggregation in selective hydrocarbon solvents. *Macromol* 26:3846, 1993.
56. ID Rubin, A Sen. Solution viscosities of ethylene-propylene copolymers in oils. *J Appl Poly Sci* 40:523–530, 1990.
57. A Sen, ID Rubin. Molecular structures and solution viscosities of ethylene-propylene copolymers. *Macromol* 23:2519, 1990.
58. D LaRiviere et al. Viscometric properties of viscosity index improvers in lubricant base oil over a wide temperature range. Part I: Group II base oil. *Lub Sci* 12(2): 133–143, 2000.
59. ML Huggins. *J Am Chem Soc* 64:2716, 1942.
60. Engine oil viscosity classification. *Soc. Automotive Engr. Surface Vehicle Standard No. J300*, rev. Dec. 1999.
61. RB Rhodes. Low-temperature compatibility of engine lubricants and the risk of engine pumpability failure. *Soc. Automotive Engr. Tech. Paper Ser. no.* 932,831, 1993.
62. BL Papke et al. Deterioration in used oil low temperature pumpability properties. *Soc. Automotive Engr. Tech. Paper Ser. no.* 2000–01–2942, 2000.
63. MA Matko, DW Florkowski. Low temperature rheological properties of aged crankcase oils. *Soc. Automotive Engr. Tech. Paper Ser. no.* 200–01–2943, 2000.
64. JA Spearot, ed. High-temperature, high-shear (HTHS) oil viscosity: Measurement and relationship to engine operation. *ASTM Special Tech. Pub., STP 1068*, 1989.
65. TW Bates. Oil rheology and journal bearing performance: A review, *Lub Sci* 2(2): 157–176, 1990.
66. RWM Wardle et al. An “in lubro” study of viscosity index improvers in end contacts. *Lub Sci* 3(1):45–62, 1990.
67. DL Alexander, SW Rein. Relationship between engine oil bench shear stability tests. *Soc. Automotive Engr. Tech. Paper Ser. no.* 872,047, 1987.
68. WJ Bartz. Influence of viscosity index improver, molecular weight, and base oil on thickening, shear stability, and evaporation losses of multigrade oils. *Lub Sci* 12(3):215–237, 2000.
69. EM Laukotka. Shear stability test for polymer containing lubricating fluids—comparison of test methods and test results. *Third Intl Symp.—The Perform. Evolution of Automotive Fuels and Lubricants*, Co-ordinating European Council Paper No. 3LT, Paris, April 19–21, 1987.
70. TW Selby. The viscosity loss trapezoid—Part 2: Determining general features of VI improver molecular weight distribution by parameters of the VLT. *Soc. Automotive Engr. Tech. Paper Ser. no.* 932,836, 1993.
71. MJ Covitch. How polymer architecture affects permanent viscosity loss of multigrade lubricants. *Soc. Automotive Engr. Tech. Paper Ser. no.* 982,638, 1998.
72. DC Kramer et al. Influence of Group II & III base oil composition on VI and oxidation stability. *National Lubricating Grease Inst. Publ. No. 9907*, Proc. 66th NLGI Annual Meeting, Tucson, AZ, Oct. 25, 1999.
73. A Rossi. Lube basestock manufacturing technology and engine oil pumpability. *Soc. Automotive Engr. Tech. Paper Ser. no.* 940,098, 1994.
74. A Rossi. Refinery/additive technologies and low temperature pumpability. *Soc. Automotive Engr. Tech. Paper Ser. no.* 881,665, 1988.

75. GA Mac Alpine, CJ May. Compositional effects on the low temperature pumpability of engine oils. Soc. Automotive Engr. tech. Paper Ser. no. 870,404, 1987.
76. SR Reddy, ML McMillan. Understanding the effectiveness of diesel fuel flow improvers. Soc. Automotive Engr. Tech. Paper Ser. no. 811,181, 1981.
77. C-X Xiong. The structure and activity of polyalphaolefins as pour-point depressants. *Lub Eng* 49(3): 196–200, 1993.
78. ID Rubin, MK Mishra, RD Pugliese. Pour point and flow improvement in lubes: The interaction of waxes and methacrylate polymers. Soc. Automotive Engr. Tech. Paper Ser.no. 912,409, 1991.
79. RM Webber. Low temperature rheology of lubricating mineral oils: Effects of cooling rate and wax crystallization on flow properties of base oils. *J of Rheology* 43(4):911–931, 1999.
80. WM Kleiser, HM Walker, JA Rutherford. Determination of lubricating oil additive effects in taxicab service. Soc. Automotive Engr. Tech. Paper Ser. no. 912,386, 1991.
81. DR Carroll, R Robson. Engine dynamometer evaluation of oil formulation factors for improved field sludge protection. Soc. Automotive Engr. Tech. Paper Ser. no. 872,124, 1987.
82. Worldwide Rubber Statistics, International Institute of Synthetic Rubber Producers, Inc., 1999.
83. Petroleum Additives Product Approval Code of Practice. American Chemistry Council, Appendix I, Sept. 2000.
84. ATC Code of Practice. Technical Committee of Petroleum Additive Manufacturers in Europe, Section H, Sept. 2000.
85. Code of Practice for Developing Engine Oils Meeting the Requirements of the ACEA Oil Sequences. ATIEL, Technical Association of the European Lubricants Industry, Appendix C, March 31, 2000.

Polymethacrylate Viscosity Modifiers

BERNARD G. KINKER

RohMax USA, Inc., Horsham, Pennsylvania, U.S.A.

1 HISTORICAL DEVELOPMENT

1.1 First Synthesis

The first synthesis of a polymethacrylate intended for potential use in the field of lubricant additives took place in the mid-1930s. The original work was conducted under the supervision of Herman Bruson, who was in the employ of the Rohm and Haas Company, and it took place in Rohm and Haas' Philadelphia Research Laboratories. Bruson was exploring the synthesis and possible applications of longer alkyl side chain methacrylates [1]. He had proposed poly lauryl methacrylate as a product that might serve as a potential thickener or *viscosity index improver* for mineral oils. The result of the work was the 1937 issuance of two U.S. patents, for "Composition of matter and process" [2] and for "Process for preparation of esters and products" [3].

1.2 First Application

Bruson's invention did indeed thicken mineral oils and was effective in increasing viscosity at higher temperatures even more so than at lower, colder temperatures. Since this behavior influences the viscosity-temperature properties or viscosity index of a fluid, these materials eventually became known as viscosity index improvers. Although polymethacrylates were successful at thickening oils, other competitive products at that time also served to increase the viscosity of mineral oils. These other polymeric materials were based on poly-isobutylene and alkylated polystyrene. The commercial success of polymethacrylates (PMA) was not at all assured. The driving force behind PMA eventually eclipsing the other commercial thickeners of the time

was PMA's value as a viscosity index improver rather than as a simple thickener of oils. In other words, PMAs have the ability to contribute relatively little viscosity at colder temperature but have a much higher contribution to viscosity at hotter temperatures. This desirable behavior enabled oil formulators to prepare multigrade oils that could meet a broader range of operating-temperature requirements. This ensured the success of PMAs into the future.

1.3 First Manufacture and Large-Scale Application

The commercial development of PMAs as viscosity index improvers lagged until the advent of World War II, when a U.S. government board rediscovered Bruson's VI improver invention. The board was charged with searching the scientific literature for useful inventions that might aid the war effort. They hypothesized about a PMA VI improver providing more uniform viscosity properties over a very broad range of temperatures, particularly in aircraft hydraulic fluids. The fluids of that era were judged to be deficient particularly in fighter aircraft because of the exaggerated temperature/time cycles experienced. On the ground the fluids could experience high temperatures from engine waste heat and then after a rapid climb to high, very cold altitudes, the fluid might experience temperatures below -40°C . After successful trials of the multigrade aircraft hydraulic fluid concept, Rohm and Haas, in cooperation with the National Research Defense Committee, rapidly proceeded to commercialize PMA VI improvers and delivered the first product, Acryloid HF, in 1942. The hydraulic fluids were quickly adopted by the U.S. Army Air Corps and were followed by other VI improvers used in hydraulic fluids and lubricants in ground vehicles.

After the war Rohm and Haas introduced PMA VI improvers to general industrial and automotive applications. Early passenger car engine oil VI improvers were first introduced to the market in 1946. The adoption of "all season" oils in the commercial market was greatly influenced by two events: first, the automotive manufacturers' viscosity specification introduction of the new designation "W" (for winter grades); and then by Van Horne's publication [4] pointing to the possibility of making and marketing cross-graded oils such as the now well-known "10W-30" as well as other cross grades. By the early 1950s use of multigrade passenger car oils was becoming widespread in the consumer market. Methacrylates played a major role in enabling the formulation of that era's multigrade engine oils. The use of PMA VI improvers has also been extended to gear oils, transmission fluids, and a broad array of industrial and mobile hydraulic fluids beyond the early usage in aircraft hydraulic fluids.

1.4 Development of Other Applications

Another important application area for polymethacrylate chemistry was in the field of *pour point depressants*. When a methacrylate polymer includes at least some longer alkyl side chains, about the same chain length as waxes normally present in mineral oil, it can interact with growing wax crystals. Waxlike side chains can be incorporated into a growing wax crystal and disrupt its growth. The net effect is to prevent the congealing of wax at the temperature where it would have occurred in the absence of a pour point depressant. Early PMA pour point depressants were used first by the military and later by civilian industry when Rohm and Haas offered such

products to the industrial and automotive markets in 1946. Although polymethacrylates were not the first materials used as pour point depressants (alkylated naphthalenes were), PMAs are probably the most predominant products in this particular application now.

Another use of wax-interactive PMAs is as refinery *dewaxing aids*. The process of dewaxing is carried out primarily to remove wax from paraffinic raffinates in order to lower the pour point of the resulting lube oil base stocks. PMA dewaxing aids are extremely wax-interactive and function as nucleation agents to seed wax crystallization and to assist the growth of relatively large crystals. The larger crystals are more easily filtered from the remaining liquid so that lube oil throughputs and yields are improved while pour points are lowered by virtue of lower wax concentrations.

Incorporating monomers more polar than alkyl methacrylates into a PMA provides products useful as ashless *dispersants* or *dispersant VI improvers*. The polar monomer typically contains nitrogen and/or oxygen (other than the oxygen present in the ester group), and its inclusion in sufficient concentration creates hydrophylic zones along the otherwise oleophilic polymer chain. The resulting dispersant PMAs (dPMA) are useful in lubricants since they can suspend in solution what might otherwise be harmful materials ranging from highly oxidized small molecules to soot particles.

PMAs have also been used in a number of other petroleum-based applications albeit in relatively minor volumes. An abbreviated list would include asphalt modifiers, grease thickeners, demulsifiers, emulsifiers, antifoamants, and crude oil flow improvers.

PMAs have been present in lubricants for about 60 years now, and their longevity stems from the flexibility of PMA chemistry in terms of composition and process. Evolution of the original lauryl methacrylate composition to include a variety of alkyl methacrylates and/or nonmethacrylates has brought additional functionality and an expanded list of applications. Process chemistry also have evolved such that it can produce polymers of almost any desired molecular weights (shear stability) or allow the synthesis of different polymer architectures.

2 CHEMISTRY

2.1 General Product Structure

Typically a polymeric methacrylate VI improver is a linear polymer constructed from three classes or three distinct lengths of hydrocarbon side chains. Simply stated, these are short-, intermediate-, and long chain lengths. A more extensive discussion is given in Section 3, but an abbreviated description is given here in order to better understand the synthesis and chemistry of methacrylate monomers and polymers.

The first class is short-chain alkyl methacrylate of one to seven carbons in length. The inclusion of such short-chain materials influences polymer coil size particularly at colder temperatures and thus influences the viscosity index of the polymer-oil solution. The intermediate class contains from 8 to 13 carbons, and these serve to give the polymer its solubility in hydrocarbon solutions. The long-chain class contains 14 or more carbons and is included to interact with wax during its crystallization and thus provide pour point depressing properties.

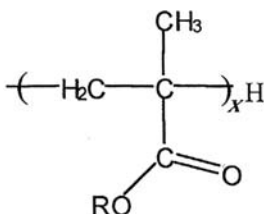


Figure 1 Polyalkylmethacrylate generalized structure.

The structure of polymethacrylates used as pour point depressants differs from that of a VI improver by virtue of typically using only two co-monomers. These are the long-chain, wax crystallization interactive materials, and intermediate chain lengths.

The selected monomers are mixed together in a specific ratio in order to provide an overall balance of the above properties. This mixture is then polymerized to provide a copolymer structure where R represents different alkyl groups and x indicates various degrees of polymerization. The simplified structure is shown in Figure 1.

2.2 Monomer Chemistry

Before discussing polymethacrylate lubricant additives, it is necessary to give an introduction to the chemistry of their parent monomers. The basic structure of a methacrylate monomer is shown in Figure 2.

There are four salient features of this vinyl compound:

1. The carbon-carbon double bond that subsequently is the reactive site in addition polymerization reactions.
2. The ester functionality adjacent to the double bond which polarizes and thus activates the double bond in polymerization reactions.
3. The pendent side chain attached to the ester (designated as R). These chains may range from an all-hydrocarbon chain to a more complex structure containing hereto atoms. A significant portion of the beneficial properties of polymethacrylates is derived from the pendant side chain.
4. The pendent methyl group attached adjacent to the double bond which serves to help shield the ester group from chemical attack, particularly as it relates to hydrolytic stability.

As mentioned, a variety of methacrylate monomers, differing by length of the pendent side chain, is normally used to construct polymethacrylate additives. The

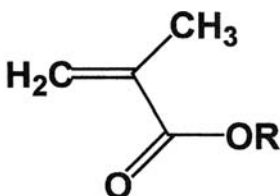


Figure 2 Alkyl methacrylate monomer.

synthesis chemistry of these monomers falls into two categories: shorter chains with four or fewer carbons and longer chains with five or more carbons. The commercial processes used to prepare each type are quite different.

The short-chain monomers are often mass-produced because of their usefulness in applications other than lubricant additives. For instance, methyl methacrylate is produced in large volumes and used primarily in production of Plexiglas® acrylic plastic sheet. It is also used in polymethacrylate lubricant additives, but the volumes in this application pale in comparison to its use in other product areas. Methyl methacrylate is generally produced by either of two synthetic routes. The more prevalent starts with acetone then proceeds through the hydrolysis of acetone cyanohydrin followed by esterification. The other route is oxidation of butylenes followed by subsequent hydrolysis and esterification.

The long-chain monomers are typically but not exclusively used in lubricant additives and can be produced by either of two commercial processes. The first is direct esterification of an appropriate alcohol with methacrylic acid. This well-known reaction is often used as a laboratory model of chemical strategies used to drive a reaction efficiently to high yield. These strategies involve a catalyst, usually an acid; an excess of one reagent to shift the equilibrium; and removal of at least one of the products, typically water of esterification again to shift the equilibrium. The relevant chemical equation is given in Figure 3.

A second commercial route to longer side chain methacrylate monomers is transesterification of methyl methacrylate with an appropriate alcohol. Typically, the reaction employs a basic compound or a Lewis base as a catalyst. The equilibrium is shifted to product by use of an excess of methyl methacrylate and by removal of a reaction product, i.e., methanol (if methyl methacrylate is used as a reactant). Figure 4 shows the reaction equation.

2.3 Polymer Chemistry

A combination of the alkyl methacrylate monomers chosen for a given product is mixed together in specific ratios and then polymerized by a solution, free-radical-initiated, addition polymerization process that produces a random copolymer. The reaction follows the classic pathways and techniques of addition polymerization to produce commercial materials [5].

These polymers are synthesized through the use of free-radical initiators. The initiator may be from either the oxygen-based or nitrogen-based families of

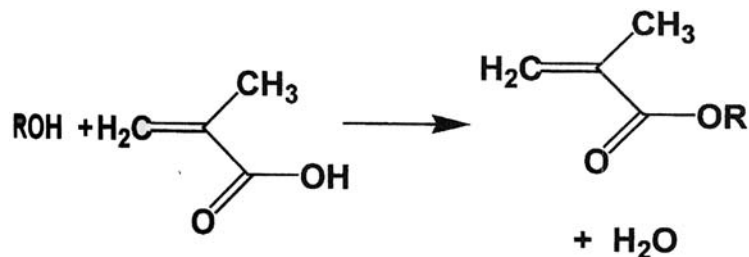


Figure 3 Direct esterification of methacrylic acid and alcohol.

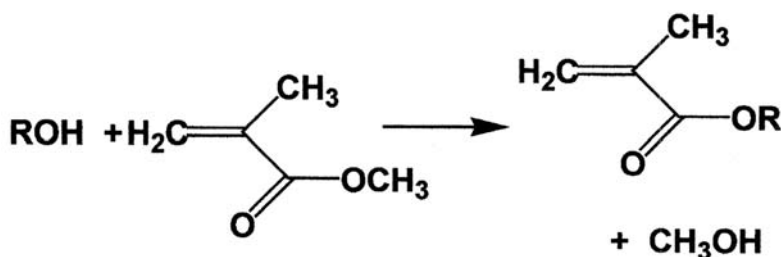


Figure 4 Transesterification of methylmethacrylate and alcohol.

thermally unstable compounds that decompose to yield two free radicals. The oxygen-based initiators, i.e., peroxides, hydroperoxides, peresters, or other compounds containing an oxygen–oxygen covalent bond, thermally decompose via homolytic cleavage to form two oxygen-centered free radicals. Nitrogen-based initiators also thermally decompose to form two molecules of free radicals, but these materials quickly evolve a molecule of nitrogen gas and thus form a carbon-centered radical. In any event, the free radicals attack the less hindered, relatively positive side of the methacrylate vinyl double bond. These two reactions are the classic initiation and polymerization steps of free-radical addition polymerization and are shown in Figures 5 and 6.

The reaction temperature is chosen in concert with the initiator's half-life and may range from 60–140°C. Generally, a temperature-initiator combination would be selected to provide an economic, facile conversion of monomer to polymer and to avoid potential side reactions. Other temperature-dependent factors are taken into consideration. Chief among these might be a need to maintain a suitable viscosity of the polymer as it is being synthesized; obviously the temperature can be utilized (as well as solvent) to maintain viscosity at a level appropriate for the mechanical agitation and pumping systems within a production unit. Excessive temperatures must be avoided in order to avoid the ceiling temperature of the polymerization.

Normally, a mixture of alkyl methacrylate monomers is used to produce a random copolymer. No special reaction techniques are needed to avoid composition drift over the course of the reaction since reactivity ratios of alkyl methacrylates are quite similar [6].

The most important concern during a synthesis is to provide polymer at a given molecular weight so as to produce commercial product of suitable shear stability. As normal for addition polymerizations, methacrylates can undergo the usual termination reactions: combination, disproportionation, and chain transfer. Chain transfer

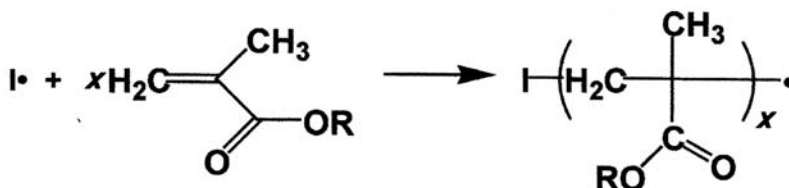


Figure 5 Free-radical initiation of methacrylate polymerization.

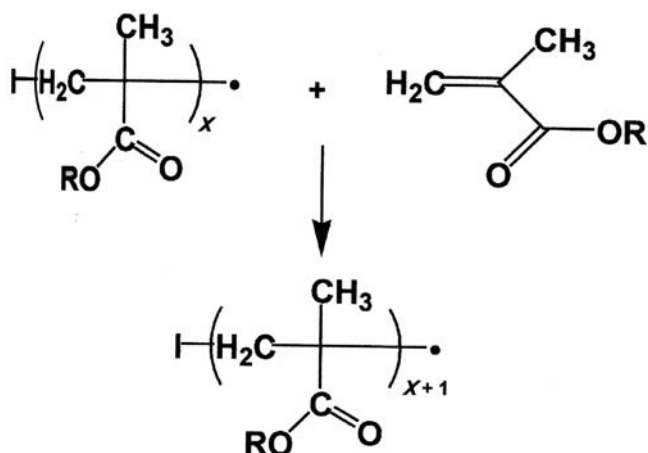


Figure 6 Addition polymerization step.

agents (CTA), frequently mercaptans, are often the chosen strategy to control molecular weight. Selection of the type and amount of chain transfer agent is done carefully, as numerous other factors influence molecular weight. Numerous factors can impact the degree of polymerization: initiator concentration, radical flux, solvent concentration, and opportunistic chain transfer with compounds other than CTA. An undesirable opportunistic chain transfer possibility is at sites along polymer chains as it leads to branched polymer chains that are less efficient thickeners. The chain transfer reaction is shown in Figure 7. In addition to chain transfer, the other usual termination reactions of chain combination and/or disproportionation occur readily with methacrylates.

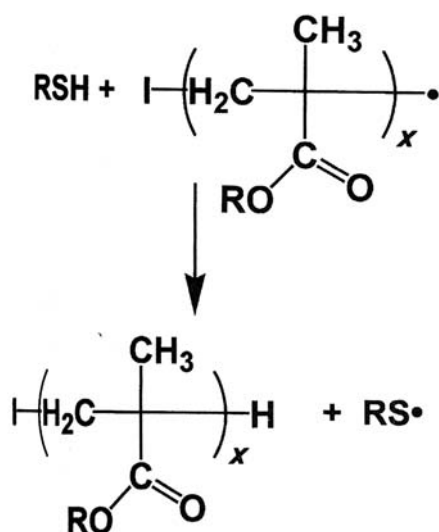


Figure 7 Termination by chain transfer.

Commercial products cover a broad range of polymer molecular weights that may range from as low as 20,000 to about 750,000 Daltons. Molecular weight is carefully controlled and targeted to produce products that achieve suitable shear stability for a given application.

Higher-molecular-weight polymethacrylates are rather difficult to handle as neat polymers. So it is necessary in almost all commercial cases to use a solvent to reduce viscosity to levels consistent with good handling properties. Similarly, it is often important to reduce viscosity as it builds during the polymerization reaction so that the sufficient agitation can be maintained. A useful solvent would (1) be non-reactive, (2) be nonvolatile (at least at the reaction temperature), (3) avoid chain transfer reactions, and (4) be consistent with the end application. It turns out that mineral oil meets the above criteria reasonably well so that a solvent choice can be made from higher-quality, lower-viscosity-grade mineral oils. Nonreactivity demands relatively higher saturate contents, but good-quality API Group I mineral oil can be used. Choice of solvent viscosity primarily depends on the end application; choices range from very low-viscosity oils (35 SUS) to light neutrals on the order of 150N. Alternatively, one can use a nonreactive but volatile solvent when mineral oil might interfere with a sensitive polymerization and then do a solvent exchange into a more suitable carrier. The amount of solvent added to commercial PMA VI improvers is sufficient to reduce viscosity to levels consistent with reasonable handling or pumping properties. This amount is dictated by polymer molecular weight, as this also greatly influences product viscosity. Generally, a higher-molecular-weight polymer requires more solvent. Commercial products may thus contain polymer concentrations over a very broad range of approximately 30 to 80 weight percent (wt. %).

Catlin first described the incorporation of dispersancy into methacrylate polymers in a 1956 patent [7]. The patent claims the incorporation of diethyl-aminoethyl methacrylate as a way of enhancing the dispersancy of VI improvers and thus providing improved deposit performance in engine tests of that era. The original dispersant methacrylate polymers utilized monomers that *copolymerize* readily with alkyl methacrylates and did not require different polymerization chemistry. Polymer grafting is also an important synthetic route to incorporate desirable polar monomers onto methacrylate polymers. Stambaugh [6] identified *grafting* of N-vinylpyrrolidinone onto PMA substrate as a route to improved dispersancy of VI improvers. Another approach is to graft both N-vinylpyrrolidinone and N-vinyl imidazole [9]. An obvious benefit of grafting is an ability to incorporate polar monomers that do not readily copolymerize with methacrylates because of significant differences in reactivity ratios. Grafting reactions are carried out after achieving high conversion of the alkyl methacrylates to polymer. Bauer [10] identified an alternate synthetic route to incorporate dispersant functionality is to provide *reactive sites* in the base polymer and then carry out a postpolymerization reaction. For example, maleic anhydride copolymerized into or onto the polymer backbone can be reacted with compounds containing desirable chemical functionality such as amines. This strategy is a route to incorporate compounds that are otherwise not susceptible to addition polymerization because they lack a reactive double bond.

The above discussion characterizes most of the chemistry used to prepare the bulk of commercial PMA products. Additional chemical strategies as well as some

novel processes and polymer blend strategies are reviewed in the Literature and Patent section

2.4 Patent Review

A review of pertinent literature and patents shows PMAs to have been the subject of numerous investigations over the course of almost 60 years. A huge body of PMA patent literature exists, and a large subset of it is related to lubricant additives. A summary from the additives-related patents suggests four major categories of investigation, which might be classified as variation of methacrylate polymer composition; incorporation of functionality to enhance properties other than rheology, e.g., dispersancy; improved processes to enhance some performance aspect; and creation of polymer blends to provide unique properties. A short discussion of only a few of the more important patents within the four categories ensues.

Since the first PMA patents [2,3], there has been a continuing search for *composition modifications* to all methacrylate polymers to improve some aspect of rheological performance. As expected, many of these efforts took place quite early in the history of PMA additive chemistry, but even today the patent literature includes teachings about all PMA compositions. For instance, highly polar PMA compositions made with high concentrations of short-chain alkyl methacrylates are useful in polar synthetic fluids such as phosphate esters to impart rheological advantages [11]. There are numerous examples of incorporating nonmethacrylates into polymers; a good example is the use of styrene [12] as a co-monomer to impart improved shear stability. However, styrenic monomers have different reactivity ratios than methacrylates and the usual processes lead to relatively low conversions of styrene. This can be overcome by a process utilizing additional amounts of methacrylate monomers near the end of the process to drive the styrene to high conversion [13].

Incorporation of *functional monomers* to make dispersant versions of PMA is discussed in the preceding section. Although the discussion features nitrogen-based dispersants, oxygen-based dispersants are also known such as hydroxyethyl methacrylate [14], and ether-containing methacrylates [15] have also been claimed. In addition to incorporating dispersant functionality, significant efforts to incorporate other types of chemical functionality such as antioxidant moieties [16] have been made.

Novel processes have been developed to improve either economics or product properties. Tight control of molecular-weight distribution and degree of polymerization can be achieved through constant feedback of conversion information to a computer control system that adjusts monomer and initiator feeds as well as temperature [17]. Coordinated polymerizations are useful in preparing alternating copolymers of methacrylates with other vinyl monomers [18]. A process to prepare continuously variable compositions can obviate the need to physically blend polymers [19].

Polymer blends of PMA and OCP VI improvers provide properties intermediate to the individual products with OCP imparting efficient thickening (and economics) and PMA imparting good low-temperature rheology. However, a physical mixture of the two VIIs in concentrated form is incompatible. This problem is overcome by use of a compatibilizer, actually a graft polymer of PMA to OCP, to make a ~70% PMA and ~30% OCP mixture compatible [20]. Very high-polymer-content products can be prepared by emulsifying the mixture so that the PMA phase is continuous in a slightly polar solvent while the normally very viscous OCP phase is in

micelles [21]. Blends of PMAs can provide synergistic thickening and pour depressing properties [22].

3 PROPERTIES AND PERFORMANCE CHARACTERISTICS

3.1 Chemical Properties

Polymethacrylates are rather stable materials and do not normally undergo chemical reactions under moderate to somewhat severe conditions. The chemical design of VI improvers or pour point depressants clearly entails avoiding reactive sites in their structure in order to provide as high a degree of stability as possible. It is expected that these types of additives are not chemically active, as they are added to alter only physical properties, i.e., viscosity and wax crystallization phenomena. When considering dispersant PMAs, which include chemistry other than alkyl methacrylate, even these have essentially the same fundamental stability as polyalkylmethacrylates. The most notable reaction of any VI improver, including PMA, is polymer shearing induced by mechanical mastication.

3.1.1 Thermal Reactions—Unzipping and Ester Pyrolysis

These reactions are known to occur with polymethacrylates, but very vigorous conditions are needed. There do not appear to be any important consequences in lubricant applications since bulk oil temperatures are normally lower than the onset temperatures of the reactions [23].

A purely thermal reaction of polymethacrylate is simple depolymerization (unzipping of polymer chains). Polymethacrylate chains at sufficiently high enough temperatures unzip to produce high yields of the original monomers. The unzipping reaction is merely the reverse of the polymerization reaction. One consequence of unzipping is that care must be taken to avoid depolymerization during polymer synthesis by simply avoiding excessive temperatures. Thus, synthesis temperatures are designed to be well below the “ceiling temperature” of the polymerization/depolymerization equilibrium. Onset temperatures for unzipping of polymethacrylates are on the order of 235°C, the temperature listed in the literature for polymethylmethacrylate depolymerization [24]. There may be a minor dependence on detailed side chain structure, but relatively little investigation has been done on higher alkyl methacrylate polymers. It is also thought that terminal double bonds on the polymer chain are the point where unzipping most readily starts. When terminal double bonds are present in the structure, they are most likely a product of termination by disproportionation.

Another potential reaction is the thermal decomposition of ester. Usually termed “beta ester paralysis,” this reaction degrades polymer side chains to yield an alpha olefin from the pendent side chain. The olefin is of the same length as the carbon skeleton of the side chain (and as long as the original alcohol used to make the monomer). The other reaction product is an acid that presumably remains in the polymer chain. The acid may react with an adjacent ester to yield alcohol and a cyclic anhydride. Another possibility is the reaction of two adjacent acid groups to form a cyclic anhydride with the elimination of a molecule of water. The pathway for the pyrolysis reaction proceeds through formation of a six-membered intermediate ring formed from a hydrogen bond of side chain beta carbon hydrogen to the ester

Table 1 Pyrolysis of PMA

Weight loss, %	Pyrolysis temperature, °C	
	290	315
2 min	—	18.7
3 min	93.2	—
5 min	93.1	94.6
10 min	94.9	96.1
15 min	96.3	97.7

carbonyl oxygen. The intermediate ring decomposes to alpha olefin and acid products [25]. Temperatures on the order of 250°C are needed to initiate this reaction.

Ester pyrolysis produces volatile alpha olefins as well as acids or anhydrides along the polymer backbone or perhaps monomeric acids or anhydrides should the reaction occur after depolymerization. The fate of acid or anhydride in the polymeric backbone would still be depolymerization under the vigorous thermal conditions present. The ultimate products are volatile under the conditions needed to initiate the reaction.

Consequences of either thermal reaction are loss of activity as a VI improver or pour point depressant and the generation of volatile small molecules. The products distill from the high-temperature reaction zone and thus offer no further opportunity for reaction. The data in Table 1 indicate the very high volatility of a PMA VI improver that has been exposed to extreme temperatures in air. There is no evidence that unzipping or ester pyrolysis is important in lubricant applications. Most lubricant applications generate temperatures far less than reaction onset temperatures; thus, these reactions are not an issue. A limited potential might exist in a micro-environment, such as if VI improver were trapped in a piston deposit where temperatures near the combustion chamber exceed onset temperature [6].

3.1.2 Oxidative Scissioning

Like any hydrocarbon when exposed to severe oxidative conditions, polymethacrylates can be subject to classic oxidation reactions resulting in polymer scissioning [23]. Scissioning yields two fragments of various lengths, each of which is obviously of lower molecular weight than the parent chain and consequently some loss of viscosity contribution. The reaction takes place at random sites along the backbone since oxidative or free-radical attack may occur anywhere along the polymer chain. Allylic, benzylic, or tertiary hydrogen are most susceptible to oxidative or free-radical attack. Methacrylates do not normally contain those structural elements; thus, the reaction is not normally an important consideration. The pyrolysis data in Table 1 would seem to support this conclusion, as scission fragments would be and large not be volatile under the conditions of the experiment.

On the whole, polymethacrylates are not prone to thermal or oxidation reactions under normal conditions of use, and there is little evidence that these reactions are important in the vast majority of PMA-based lubricant applications.

3.1.3 Mechanical Shearing and Free-Radical Generation

A well-known, important degradation reaction of any VI improver including polymethacrylates is mechanical shearing. Although polymer shearing begins as a physical process, it does generate free radicals. For each polymer chain rupture, two transitory carbon-centered free radicals are generated. In lubricants, the free radicals are apparently quickly quenched by presumably abstracting hydrogen from the surrounding hydrocarbon solvent or perhaps by the antioxidants in formulated lubricants. Overall, there appear to be few if any further chemical consequences. On the other hand, there are important viscometric consequences since the rupture leads to two lower-molecular-weight fragments that provide a reduced viscosity contribution. The shearing process is initiated through the concentration of sufficient energy within the polymer chain to induce homolytic cleavage of a carbon-carbon bond in the backbone of the polymer. The susceptibility of the polymer to mechanical shearing is not related to its chemical structure; rather it is very clearly a function of polymer molecular weight or even more appropriately to the end-to-end distance of the polymer chain [26]. Overall VI improver shear stability, while an important physical process, does not appear to carry any appreciable chemical consequences. Further discussion can be found in the section on the effect of structure on physical properties.

3.1.4 Hydrolysis

Polymethacrylates are not very susceptible to hydrolysis reactions; however, the question of hydrolytic stability is often posed because of the presence of the ester group. In the polymeric form methacrylate ester groups are quite stable since they are well shielded by the surrounding polymer and pendant side chains. The immediate chemical environment surrounding the ester is definitely hydrophobic and not conducive to compounds that participate in or catalyze hydrolytic reactions. Extraordinary measures can be used to induce hydrolysis; for instance, lithium aluminum hydride hydrolyzes polymethacrylates to yield the alcohols from the side chain. Nevertheless, there is no evidence that PMA hydrolysis is of any significant consequence in lubricant applications.

3.2 Physical Properties

The paramount properties of polymethacrylates are those associated with their use in solution as pour point depressants (PPDs), VI improvers, or dispersants. The dispersants may also be utilized for their VI improver or thickening properties, while in some cases thickening properties are not needed and the molecules are used solely as dispersants. The useful properties of PMAs are related to both their physical nature (primarily molecular weight) and to their chemical nature (primarily side chain structure).

3.2.1 Pour Point Depressants

PPDs are used to modify and control wax crystallization phenomena in paraffinic mineral oils. As temperature decreases, waxy components begin to form small, plate-like crystals. The plates eventually grow together to form an interlocking network that effectively traps the remaining liquid. Flow ceases unless a force strong enough to break the relatively weak wax gel matrix structure is applied. Control of wax

crystallization is often described as pour point depressancy since one of the quantifiable effects is to reduce the ASTM D 97 pour point. The pour point test is fairly archaic as it utilizes a very rapid cooldown to measure only flow versus no-flow conditions. PPDs also control wax crystallization during a variety of slower, more realistic cooling conditions that better favor crystal growth. A PPD is used to maintain fluidity of lubricants under a variety of cooling conditions in order to expand a lubricant's operating temperature window into colder regimes. How much the operating window is expanded is a complex function of wax chemistry and concentration in base oil, the presence or absence of other waxy additives, the cooling conditions, the final cold temperature, and, of course, PPD chemistry and concentration [27].

PPDs do not affect either the temperature at which wax crystallizes from solution or the amount of wax precipitate. Pour point depressants do co-crystallize on the edges of the growing wax plates. Thus, the growing wax crystal is attached to the polymer via side chain, and then because of the presence of the molecularly large polymer backbone, crystal growth is sterically hindered in-plane. Further growth is redirected in a perpendicular direction, resulting in the formation of more needlelike crystals. Thus, the usual tendency to form a three-dimensional structure based on platelike crystals is disrupted, and wax gel matrices are prevented at least temporarily. At exceedingly low temperatures, oils may eventually become so viscous as to appear to cease flowing, but this is irrespective of wax issues [28].

Polymethacrylates were the first polymeric pour point depressants, and they remain the most predominant chemistry in this application enjoying a majority of the worldwide market. The reason for this success is related to the molecular structure as shown in Figure 8 and its inherent chemical flexibility in terms of polymer chain length and even more importantly the ability to include various side chain structures and at almost any concentration.

In Figure 8, R1 and R2 represent two different lengths of alkyl side chains; one is wax-interactive and the other is "neutral," or noninteractive with wax. But the side chains are actually complex mixtures of alkyl groups that may be anywhere from 1 to over 20 carbons. The longer carbon side chains are intended to interact with wax; in order to do so, they should be linear and at least 14 carbons atoms in length. The interaction of a waxy alkyl side chain with wax intensifies as its length increases. However, shorter chains are added to serve as inert diluents, thereby ensuring a controlled degree of wax interaction or to act as spacers between the longer side chains so as to better fit into crystal lattice structures.

Pour point depressancy is independent of molecular weight over a large range and degree of polymerization that may vary from about 200 to near 3000. But it is important to achieve a minimum degree of polymer backbone size to provide enough steric hindrance to crystal growth as described above.

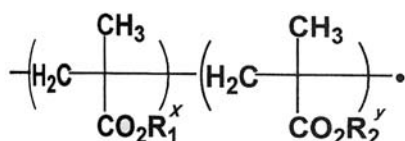


Figure 8 PMA pour point depressant.

Table 2 PPD Response in Different Base Oils

Wt. %	Base stock 1*	Base stock 1	Base stock 2	Base stock 2
	PPD 1 Low WIF	PPD 2 High WIF	PPD 1 Low WIF	PPD 2 High WI
None	-18	—	-12	—
0.05	-24	-21	-18	-18
0.10	-33	-30	-21	-27
0.20	-36	-30	-27	-33

*ASTM D 97 pour point, °C.

The optimum positive interaction with wax requires a careful balance of the waxy alkyl groups in terms of both type and concentration. This thought is sometimes expressed as a function known as the “wax interaction factor” (WIF) that takes into account the amount of each alkyl group that interacts with wax and the strength of the interaction. Since mineral oils contain a distribution of wax chain lengths, PPDs often contain a distribution of waxy side chains to best interact with wax in a specific situation. As the wax structure and content change because of different base stocks and/or additives, then a different PPD with a different WIF may be the optimum. This effect is shown in Table 2, where different base stocks with different wax chemistries and concentrations respond differently to PPDs with different WIF.

Finished formulations often respond differently to PPDs than do the base oils used to make the fully formulated oils. For example, in the MRV TP-1 two different 150N base stocks respond to PPD 3: one (A) with some yield stress and the other (B) with acceptable properties; however, when these same base stocks are additized (same DI and VII), they respond in an opposite way. The SAE 10W-40 based on oil A has passing rheology, while the SAE 10W-40 based on oil B is a clear failure. PPD 4 with different WIF does provide passing results with the formulation based on oil B. These data are shown in Table 3.

3.2.2 Viscosity Index Improvers

Viscosity index improvers (VII) are used to achieve the advantages of multigrade lubricating oils in numerous applications including crankcase engine oils, automatic-transmission fluids, high VI hydraulic fluids, gear oils, and other lubricants

Table 3 Comparison of PPD Response in Base Stocks Versus Fully Formulated Oils*

PPD treat rate 0.1 Wt. %	Base stock A (150N)	Base stock A + DI and VII (SAE 10W-40)	Base stock B (150N)	Base stock B + DI and VI (SAE 10W-40)
PPD 3	31,100/35	39,700/<35	26,500/<35	62,000/70
PPD 4	—	—	28,100/<35	35,800/<35

*MRV TP-1 Viscosity, -30°C (cP), and yield stress (Pa).

used primarily outdoors. Ideally, VIIs provide increased viscosity at higher temperatures and minimal viscosity contribution at lower temperatures [29]. VI improvers and viscosity modifiers are high-molecular-weight, oil-soluble polymers. Current commercial chemistries are based on either of two chemical families: (1) hydrocarbons, for example, ethylene-propylene copolymers; (2) the other family contains ester functionality such as polymethacrylates. There are other examples of each chemical family. PMA chemistry dominates applications where high viscosity index, or more succinctly, superior low-temperature properties, is required [26]. These benefits can usually be observed in typical lubricant industry low-temperature, low-shear-rate rheology tests such as MRV TP-1, Scanning Brookfield, and ASTM D 2983 Brookfield as well as numerous others. PMA VI improvers thicken oils at higher temperatures but contribute relatively little low-temperature viscosity because of their molecular weight (size) and their detailed chemical composition, specifically the structure and concentration of pendent side chains. Molecular size influences thickening at all temperatures, and chemistry influences relative solubility and low-temperature thickening. In addition to rheological functions, PMA VIIs can be synthesized to contribute other useful functions such as point depressancy and dispersancy.

Thickening properties for any chemical class of VI improver or viscosity modifier are related to the immensely greater molecular size compared to that of the solvent or base stock in which it is dissolved. The long polymeric strand, the backbone of the polymer, is configured in a random coil shape. The size of the coil, or more appropriately its hydrodynamic volume, is proportional to polymer molecular weight as a first approximation, but more exactly to the cube of the root mean-square end-to-end distance of the polymer. In the lattice theory of viscous flow, segments of polymer molecules fill holes in the lattice (constructed of all surrounding molecules) and thereby limit the ability of smaller molecules to participate in movement through the lattice [26]. The degree of viscosity increase depends on coil size; thus, higher-molecular-weight polymers provide more thickening. The overall viscosity of a polymer-thickened solution is related to polymer concentration and molecular weight through Eq. (1):

$$\ln \eta = KM_v^a c - k''(M_v^a)^2 c^2 + \ln \eta_0 \quad (11.1)$$

where

M_v = VI improver viscosity average molecular weight.

c = VI improver (or thickener) concentration.

η_0 = solvent viscosity.

and the exponent a relates to solubility of the specific polymer chemistry, solvent, and temperature.

For a PMA VI improver in solution, the coil size expands and contracts with temperature [30]. At lower temperatures PMA is, on a relative basis, poorly soluble in oil. This is not meant to say that PMA precipitates from solution, but the relative solubility results in a contracted, smaller-volume polymer coil, which has a low-viscosity contribution. As temperature increases, solubility improves, and polymer coils eventually expand to some maximum size and in so doing donate more and

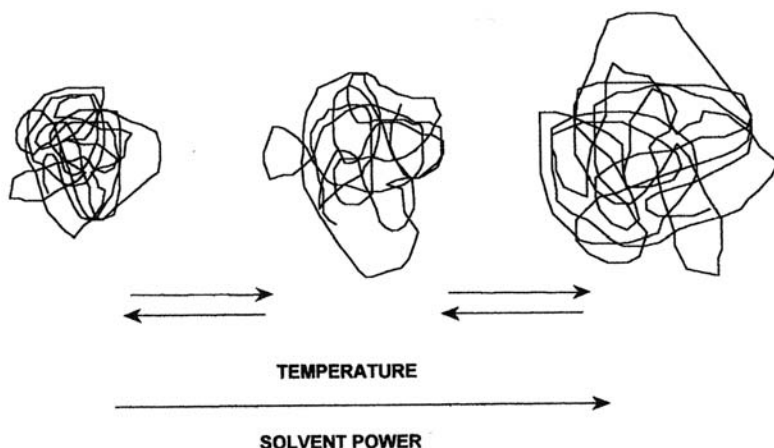


Figure 9 PMA coil expansion.

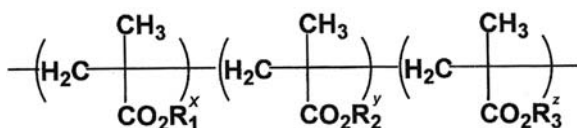


Figure 10 PMA VI improver structure.

more viscosity. The process of coil expansion is entirely reversible as coil contraction occurs with decreasing temperature (see Figure 9). In contrast, nonpolar polymeric thickeners are well solvated by oils at all temperatures and experience far lower degrees of coil expansion/contraction [31]. These solubility factors relate to the value of the exponent a in the thickening Eq. (1) and for PMA are a function of the detailed side chain chemistry normally constructed from three classes of methacrylic ester chain length: short, intermediate, and long alkyl chains. This structural concept of three distinct chain lengths is represented in Figure 10.

Usually a PMA with an average side chain length of about eight carbons will be soluble in oil, even down to very low temperatures. So an intermediate chain length is used to provide overall oil solubility and normally is selected from linear or branched chains composed of 8 to 14 carbons. The longer chains consisting of more than 14 carbons are incorporated to be wax-interactive as described above in the section on pour point depressants. The very short chains, usually C1 or C4, are used to balance the composition and make the average chain length about nine carbons or slightly more than the minimum of eight carbons needed for solubility. To a first approximation the average chain length will determine viscosity and temperature properties rather than the fine detail of chain length and structure. Including pour point depressancy into PMA VIIs may involve compromises since

optimized wax interaction may not be possible in the many base stocks where the VII is employed. VII treat rates are quite high compared to PPD and may simply overwhelm wax crystallization phenomena, thereby obviating any lack of optimized wax interaction.

Commercial polymethacrylate VI improvers are available in various chemical compositions and molecular weights ranging from about 10,000 to 800,000 Daltons. The higher-molecular-weight materials are the most efficient thickeners and provide the greatest VI lift but are also the most susceptible to shearing effects. Selection criteria should focus on the impact of the application on stability as well as thickening efficiency and VI lift.

Shearing effects, either temporary or permanent, are related to polymer backbone molecular weight. Unfortunately, high-molecular-weight polymers are subject to shear thinning and mechanical mastication, both of which result in loss of thickening. The former is temporary, while the latter is permanent.

Temporary viscosity loss occurs when polymer molecules become oriented along the axis of flow at sufficiently high shear rates, normally on the order of 10^4 sec^{-1} . Polymer shape changes from a spherical coil to an elongated configuration that occupies a smaller hydrodynamic volume and thus contributes less viscosity. With further increases of shear rate, molecules increasingly deform, leading to a corresponding greater loss of viscosity contribution until maximum distortion is reached. Within the lubricant community, non-Newtonian, shear thinning behavior is better known as “temporary loss of viscosity” since the process is reversible upon removal of high shear rates. Distorted polymer molecules resume random coil shapes, reoccupy original hydrodynamic volumes, and contribute viscosity as before the application of high shear rate. The degree of temporary viscosity loss depends on the level of shear stress and the molecular weight of the polymer. Because of their small coil sizes, low-molecular-weight polymers are less susceptible to shear thinning.

The temporary viscosity loss of PMAs is directly related to molecular weight, or, more appropriately, to backbone molecular weight. PMAs are not associative thickeners and do not experience viscosity losses through loss of molecular associations in high shear stress fields. Any loss of viscosity is related merely to molecular size and the distortion of the molecules to occupy lower hydrodynamic volumes. [Figure 11](#) is compiled with data taken from a set of SAE 10W-40 oils blended to constant kinematic viscosity ($14.5 \text{ mm}^2/\text{sec}$) and constant CCS with the same compounding materials except VII. Three chemically equivalent dispersant PMA VIIs differing in molecular weight were used in the formulations. The resulting high-temperature, high-shear-rate (HTHS) viscosities are clearly a function of polymer molecular weight.

Permanent viscosity loss via mechanical degradation occurs when very high shear stresses, perhaps coupled with turbulent flow, can lead to extreme polymer coil distortion and concentrate enough vibrational energy to cause polymer rupture. Cavitation probably also plays an important role by producing intense velocity gradients. Polymer rupture occurs through cleavage of a carbon-carbon bond statistically near the middle of the polymer chain, leading to two molecules each having approximately half the molecular weight of the original molecule. [Figure 12](#) represents molecular elongation and rupture concepts. The total hydrodynamic volume of the two smaller molecules is less than that of the single parent molecule, resulting in a lower viscosity contribution. Since bond scission is not reversible, the viscosity

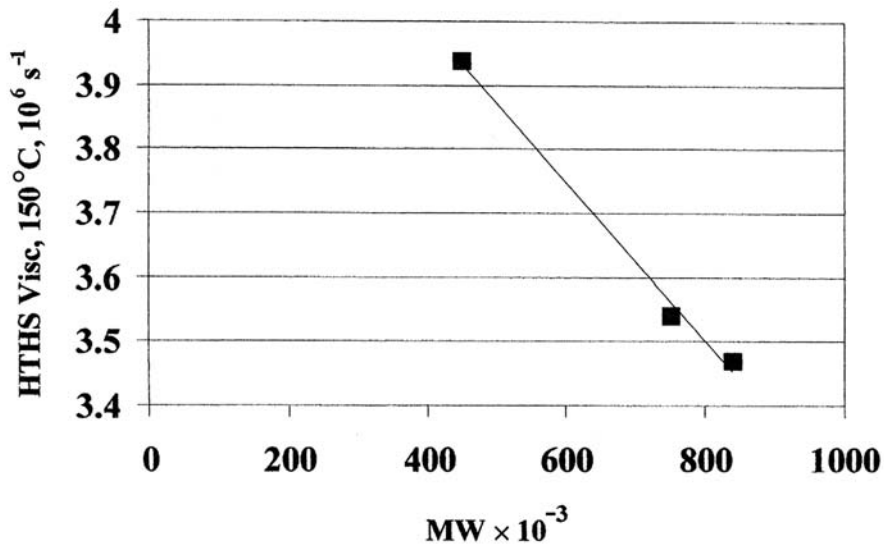


Figure 11 Relationship of PMA VI improver molecular weight to temporary shear stability. (SAE 10W-40 oils all blended to 14.5 mm² sec at 100°C.)

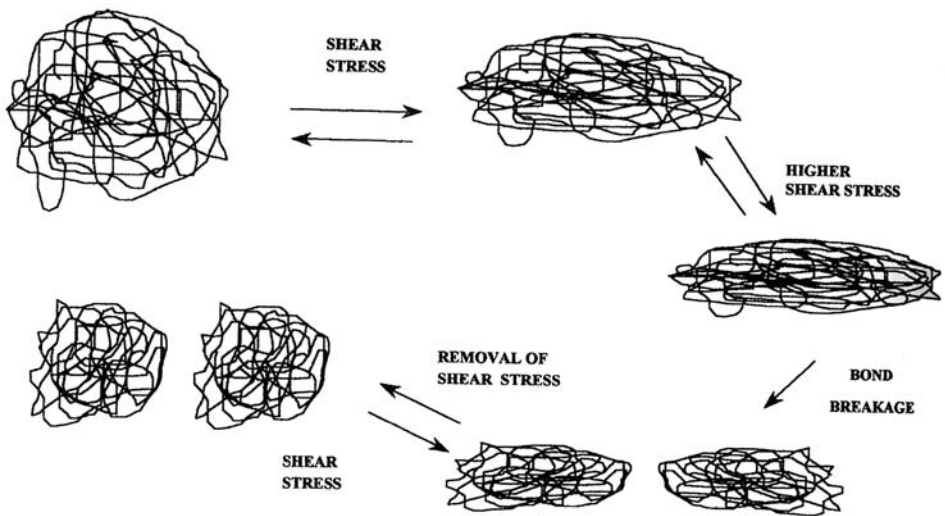


Figure 12 Temporary and permanent shearing of polymer.

loss is permanent. Higher-molecular-weight polymers are more susceptible to distortion and mechanical degradation, while polymers of sufficiently low molecular weight may not even undergo permanent shearing. The sheared polymer molecules are typically of sufficiently lower molecular weight that are not normally susceptible to further degradation, so the degradation process is self-limiting.

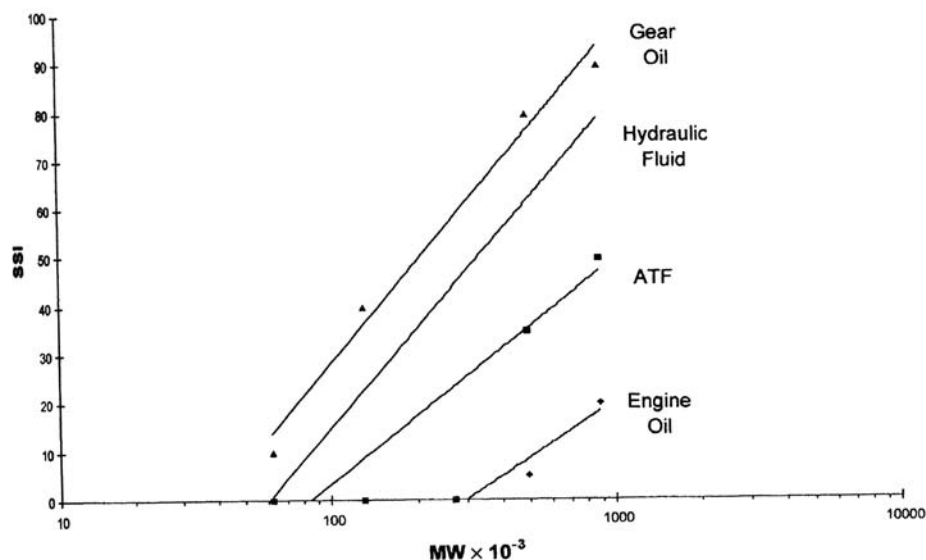


Figure 13 Relationship of shear stability index to PMA VII molecular weight and shear severity by application.

As with shear thinning phenomena, PMAs of sufficient molecular weight are subject to mechanically induced permanent loss of viscosity. Again, the amount of viscosity loss is a reasonably straightforward function of molecular weight (size) in solution for a given shearing force. Molecular-weight distribution plays a secondary role. If MW distribution were skewed to larger fractions of high-MW polymer, then the loss of viscosity would be greater than that of a polymer of similar average MW but with a Gaussian distribution. It should also be noted that different applications can create very different shear stresses and, because of this, viscosity losses of polymers of any given MW vary by application. The net result is that viscosity loss to a first approximation is directly related to molecular weight and to the amount of shearing force in a given application or laboratory bench test. The relationship of shear stability index to polymer MW and shearing severity by application is shown in Figure 13 for a set of PMA VIIs [32].

Dispersancy may be incorporated into PMA base chemistry through incorporation of a monomer that normally contains a heteroatom to create a polar zone along the polymer chain. Usually the heteroatom is nitrogen from an amine, amide, or lactam, but oxygen is sometimes used. As previously discussed, incorporation can be achieved through copolymerization, grafting, or postreaction of a reactive species into or onto the polymer. The resulting polar region serves to attract and peptize small polar molecules or particles, i.e., oxidized oil, oxidized fuel, or even soot. These undesirable materials are often unintentional byproducts of combustion or oxidation of the lubricant. Left undispersed, the small molecules may undergo further chemistry to form harmful deposits while particulate matter may become a source of abrasive wear.

Table 4 Engine Test Performance of Dispersant PMA VII Versus Nondispersant PMA VII in SAE 5W-30 API SG Formulations*

PMA VIIs (45 SSI)	Ave. sludge	Ave. varnish	Ave. cam wear
Dispersant	9.23	6.25	1.5
Nondispersant	4.55	4.56	5.8

*Sequence VE test—Summary data (average from six tests).

The PMA dispersants are used as both standalone products in some applications and as dispersant VI improvers. An example of an ashless dispersant PMA is their use in SAE J1899 piston aircraft engine oils. PMA dispersants can be employed to boost the overall dispersancy of a formulation in order to enhance specific performance features. Dispersant VIIs have often been used in engine oils either to supplant some of the traditional ashless dispersants or simply to enhance dispersancy (in addition to impacting the usual rheological properties). Table 4 contains data from Sequence VE engine tests of a SAE 5W-30 API SG oil made from dispersant PMA VII of 45 Bosch SSI and another SAE 5W-30 oil containing all the same compounding materials except that it contained a nondispersant PMA VII also of 45 Bosch SSI. The results were averages from six engine tests. Clearly, the dispersant VII provides enhanced dispersancy relative to its nondispersant analog.

4 MANUFACTURER, MARKETING, AND ECONOMICS

4.1 Manufacturers and Marketers

The following companies offer polymethacrylate additives for sale:

Ethyl Petroleum Additives, Inc.
330 South Fourth Street
P.O. Box 2189
Richmond, Virginia, 23219

Infineum UK Limited
P.O. Box 1
Milton Hill
Abingdon
Oxfordshire
OX 13 6BB United Kingdom

Nippon NSC Ltd.
Specialty Synthetic Polymers
Ginza Wall Bldg.
6-13-16, Ginza, Chuo-ku
Tokyo 104-0061, Japan

The Lubrizol Corporation
29400 Lakeland Boulevard
Wickliffe, Ohio, 44092-2298

Table 5 Polymethacrylate Product List Prices

Product description	Application	US\$ per pound
VII—45 SSI	Engine oil	0.87
Dispersant VII—45 SSI	Engine oil	1.15
Dispersant VII—25 SSI	Engine oil	1.43
VII—15 SSI	Hydraulic fluid	1.74
VII—30 SSI	Hydraulic fluid	1.64
PPDs	Various	1.47–2.10

Notes: SSI values for engine oil application is from ASTM D 6278 (30 Pass Bosch Diesel Injector). SSI values for hydraulic fluid applications are from ASTM D 5621 40-min sonic shear).

Source: Courtesy of RohMax USA.

RohMax Additives GmbH
Kirschenallee
D-64293 Darmstadt
Germany

Sanyo Chemical Industries, Ltd.
11-1, Ikkyo Nomoto-cho, Higashiyama-ku
Kyoto 605-0995, Japan

Toho Chemical Industry Co. Ltd.
6-4, Akashi-Cho, Chuo-Ku
Tokyo 104-0044, Japan

Within the realm of lubricant additives, NSC primarily offers polymethacrylate VI improvers and pour point depressants. RohMax, Sanyo Kasei, and Toho, although focused on polymethacrylates, do offer other product types to the lubricant and oil-refining industries. Ethyl, Infineum, and Lubrizol offer polymethacrylates as well as other additives types and additive packages for lubricants.

4.2 Economics and Cost-Effectiveness

A few typical list prices for a range of VI improver products differing application and shear stability are given in Table 5. Also included are typical list prices for some typical pour point depressants. Of course, one must know an additive's treat rate in order to do a meaningful economic study. While this is true for any additive type or chemistry, it is particularly true for VI improvers as their treat rates may vary widely by the chemistry of the additives as well as by viscosity grade of the treated oil. In addition, if the VI improver brings value-added features such as pour point depressancy or dispersancy, then the economic credit for these features must be accounted for in net treat cost calculations.

The cost-effectiveness of polymethacrylate VI improvers varies widely by application. When enhanced low-temperature requirements, high viscosity index, and/or

excellent shear stability are requirements, then polymethacrylates often enjoy excellent cost competitiveness. Examples of these applications are automatic-transmission fluids, multigrade hydraulics, and the lower SAE W gear oil grades. In these situations it may often be impractical to employ other VI improver chemistries because of some technical deficiency.

In engine oils where the above technical criteria are not as stringent, polymethacrylate VI improvers are often at a cost disadvantage. Fundamentally, PMAs are less efficient thickeners than many competitive hydrocarbon VI improvers such as olefin copolymers or polyisoprenes. VI improver thickening is a function of polymer backbone molecular weight (actually the unperturbed root mean-square end-to-end distance), but only a minor portion (about 15%) of PMA molecular weight is in the backbone compared to an OCP with about 80–90% backbone MW. Recall that a large majority of the molecular weight of a polymethacrylate is found in the pendant side chain simply to provide oil solubility. So, when comparing a PMA to an OCP of similar total MW, the PMA clearly has a shorter end-to-end distance and is clearly less efficient. In situations where a PMA may bring some unique value to the formulation such as additional dispersancy (i.e., soot control in HDDEO) or superior low-temperature properties, then these technical advantages may make PMA more economic.

For pour point depressants, it is again difficult to assign some typical treat rate. PPD concentrations may vary widely due to numerous factors including the types of base stocks employed, the impact of other additives on desired properties, and even the types of cold-temperature tests used for a given application. In addition to efficiently pour depressing any given lubricant, PPD economics involve the commercial reality that as few as possible, more likely a single PPD, would be favored at a blend site. Thus, performance robustness in a variety of formulations is highly leveraged. Methacrylates with their inherent flexible chemistry can be well tuned to meet this objective and thus often provide a further degree of cost-effectiveness. Overall it is difficult to quantify cost-effectiveness in a simple way; however, PMA PPDs are believed to be the most widely used chemistry in this application and command over 50% of the world market. A simple conclusion is that polymethacrylates are indeed cost-effective in this application.

4.3 Other Incentives

Competitive pressures from other chemistries will always remain high in the modern, global, cost-competitive economy. The persistence of polymethacrylates over many decades is to some degree a compliment to their adaptability and to their ability to succeed in those applications with demanding rheological specifications. The continued success of polymethacrylates depends on two aspects. The first is clearly the market's need for higher rheological performance. The second is the ability of polymethacrylates to deliver higher rheological value and potentially other nonrheological properties when needed. Given the needs described above, polymethacrylates will almost assuredly continue to evolve to better provide rheological properties, produce more cost-effective polymer ingredients, and serve as a delivery substrate for other nonrheological properties (i.e., dispersancy).

5 OUTLOOK AND TRENDS

5.1 Current and Near-Term Outlook

The outlook for polymethacrylate *VI improvers* is to a large degree tied to multigrade fluid rheology requirements of current or evolving mechanical equipment. The historic viscometric trends over the past decade have featured both improved low-temperature viscosity and shear stability specifications. This is best exemplified in the area of automatic-transmission fluid specifications. But many other multigrade fluid specifications have experienced varying degrees of improved low-temperature viscosity and/or shear stability requirements. In addition, enhanced shear stability alone implies higher polymer treat rates (in a given base stock) and greater difficulty meeting low-temperature viscosity limits. The net effect of these specification changes has been to solidify the use of PMA (or dPMA) VI improvers in those applications with more demanding low-temperature specifications or where upgrades to shear stability are required. Along with the trend to better shear stability, VI improver volume expands, since higher VI improver treat rates are required.

It would seem that these same trends should continue into the future. In those applications where PMA VI improvers are advantaged, equipment trends and environments in which the equipment operates continue to evolve so as to require enhanced fluid properties. As an example, equipment such as more complex step transmissions, continuously variable transmissions, higher-pressure hydraulic pumps, and gearboxes in thermally demanding environments will probably create needs for fluids with many enhanced requirements including excellent shear stability/low-temperature properties. Presuming this scenario to be true, then one would speculate that PMA chemistry will continue to evolve to meet these new rheological demands created by equipment and also new base stocks needed to formulate suitable fluids. In short, the use of PMA VI improvers will most likely continue to be reinforced where it is already established. In applications such as engine oils where PMA VI improvers are not needed for value-added features and/or are not cost-competitive, then it is not easy to foresee significant future use unless specifications change significantly to require the use of PMA.

The outlook for polymethacrylate *pour point depressants* is obviously tied to low-temperature rheology specifications as well as to the waxy nature of lubricant fluids and additives. This latter point strongly suggests that wax chemistry and wax concentration in base stocks will continue to be of paramount importance to the future use of pour point depressants. In addition, the complex interaction of base stock wax and other additives with a waxlike character will also strongly influence pour point depressant chemistry. Further evolution of base stocks with different wax chemistry and evolution of additives with a waxlike character will continue to emphasize development of new pour point depressants that control such unique crystallization phenomena. Since PMA can be easily modified to provide various types and levels of wax crystallization interaction, their future as pour point depressants would appear to be assured.

For polymethacrylate *dispersant VI improvers* (or disregarding thickening effects) *dispersants*, the outlook is not as clear. In applications where these materials are currently used as dispersants, their use will probably continue for the foreseeable future with little change in terms of chemistry or commercial volumes. Examples of these applications are (1) as ashless dispersants in piston aircraft engine oils and (2)

to disperse non-oil-soluble compounds in mineral oils. There are potentially important commercial possibilities if industry needs for dispersancy reach higher levels. One example is enhanced soot dispersancy in future diesel engine oils where higher soot loadings are created by engines equipped with EGR. Another potential could be minimization of engine oil cold cranking simulator (CCS) viscosities since dPMA contributes less to CCS viscosity than traditional polyisobutylene-based dispersants. It is unclear if either of these possibilities will become reality, so it remains unclear if the use of dPMA will expand.

5.2 Long-Term Outlook

Just as for many other additives and base stocks, the future of PMAs depend on the rheological appetites of future equipment. In the absence of revolutionary equipment development, longer-term trends will continue to be driven by environmental and consumer concerns. Most simply stated, this translates to emissions reductions, fuel efficiency, and longer drain intervals. These three concerns certainly apply in varying degrees to all multigrade fluids: engine oils, transmission fluids, or hydraulic fluids. Lubricants will most likely continue their migration to enhanced but traditional properties. In this case PMAs will most likely retain their market niches, but PMAs will also continue to evolve to accommodate improvements in shear stability, wax interaction, and perhaps dispersancy.

Also, the future use of PMAs depends intimately on future base stocks. For instance, should entirely synthetic (PAO) base stocks be the choice of the future to provide enhanced properties, then this would obviate the use of any pour point depressants, as these base stocks are waxfree. Additives like PMA pour point depressants may be an enabling factor in the use of newer base stocks such as API Group II+ or API Group III base stocks in meeting performance goals that match or are quite similar to those of API Group IV base stocks.

For the case of revolutionary equipment changes such as ceramics engine parts or vehicles based on batteries, fuel cells, or hybrids, lubricant needs will surely undergo a similar revolution. Most of these changes would radically alter the chemical and physical character and/or volumes of lubricants since the interesting but hostile environment of an internal combustion engine would no longer dictate the complex chemistry of engine lubricants. As engine lubricant volumes declined, surely all PPDs and VIIs would experience a proportional decline. However, in the other applications where PMA VI improvers are employed, such radical equipment changes do not appear to be on the horizon.

REFERENCES

1. S Hochheiser. Rohm and Haas, History of a Chemical Company. Philadelphia: University of Pennsylvania Press, 1986, p 145.
2. U.S. Patent 2,001,627 (1937, Rohm and Haas Co.).
3. U.S. Patent 2,100,993 (1937, Rohm and Haas Co.).
4. WL Van Horne. Polymethacrylates as viscosity index improvers and pour point depressants. *Ind Eng Chem* 41(5):952–959, 1949.
5. FW Billmeyer. *Textbook of Polymer Science*. New York: Wiley-Interscience, 1971, pp 280–310.

6. RL Stambaugh. Viscosity index improvers and thickeners. In RM Mortimer, ST Orszulik, eds. *Chemistry and Technology of Lubricants*. London: Blackie Academic & Professional, 1997, pp 144–180.
7. U.S. Patent 2,737,496 (1956, E.I. Du Pont de Nemours Co.).
8. U.S. Patent 3,506,574 (1970, Rohm and Haas Co.).
9. U.S. Patent 3,732,334 (1973, Rohm GmbH).
10. British Patent 636,998 (1964, Rohm and Haas Co.).
11. U.S. Patent 5,863,999 (1998, Rohm and Haas Co.).
12. U.S. Patent 4,756,843 (1998, Institute Francais du Petrol).
13. U.S. Patent 6,228,819 (2001, Rohm and Haas Co.).
14. U.S. Patent 3,249,545 (1966, Shell Oil).
15. U.S. Patent 3,052,648 (1962, Rohm and Haas Co.).
16. U.S. Patent 4,790,948 (1988, Texaco Inc.).
17. E.P. Patent 569, 639 (1993, Rohm and Haas Co.).
18. Japanese Patent 4,704,952 (1972, Sumitomo Corp.).
19. U.S. Patent 6,140,431 (2000, Rohm and Haas Co.).
20. U.S. Patent 4,149,984 (1979, Rohm GmbH).
21. U.S. Patent 4,290,925 (1981, Rohm GmbH).
22. Great Britain Patent 1,559,952 (1977, Shell, Intl.).
23. JP Arlie, J Dennis, G Parc. Viscosity index improvers 1. Mechanical and thermal stabilities of polymethacrylates and polyolefins. IP Paper 75-005, Inst. Petr., London, 1975.
24. J Branderup, EH Immergut, eds. *Polymer Handbook*. New York: Interscience, 1966, pp. V-5–V-11.
25. J March. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*. New York: McGraw-Hill, 1968, p 747.
26. BG Kinker. Automatic transmission fluid shear stability trends and viscosity index improver trend. Proc. 98 Intl Symp. Tribology of Vehicle Trans. Yokohama, 1998, pp 5–10.
27. BG Kinker. Fluid viscosity and viscosity classification. In G Totten, ed. *Handbook of Hydraulic Fluid Technology*. New York: Marcel Dekker, Inc., 2000, pp 318–329.
28. RohMax Publication RM-96 1202. *Pour Point Depressants, A Treatise on Performance and Selection*, Horsham, PA, 1996.
29. P Neudoerfl. State of the art in the use of polymethacrylate VI improvers in lubricating oils. In WJ Bartz, ed. 5th Intl. Coll., *Additives for Lubricants and Operations Fluids*, vol. 11, Technische Akademie Esslingen, Ostfildern, 1986, pp 8.2-1–8.2-15.
30. TW Selby. The non-Newtonian characteristics of lubricating oil. Trans. ASLE 1:68–81, 1958.
31. HG Mueller, G Leidigkeit. Mechanism of action of viscosity index improvers. Tribol Intl 11(3): 189–192, 1978.
32. RJ Kopko, RL Stambaugh. Effect of VI improver on the in-service viscosity of hydraulic fluids. SAE Paper 75,069,319, 1975.

Tackiness and Antimisting Additives

FREDRIC A. LITT

Functional Products Inc., Macedonia, Ohio, U.S.A.

1 WHICH POLYMER SOLUTIONS ARE TACKIFIERS?

Various classes of additives are comprised of polymers dissolved in oil. Some of these, such as cold-flow improvers, dispersants, and antifoams, are relatively low-molecular-weight polymers with particular active side group (or rarely, main-chain sequence) chemical functions that provide the desired activity. For these additives, the polymer serves as a “spacer” or “support” for the functional groups, although it may also be used to target a desired solubility. Generally, these additives have molecular weights below about 100,000.

Polymers of higher, molecular weight are used as additives that bring about a desired viscometric or viscoelastic effect. Most viscosity index improvers have molecular weights between about 100,000 and 250,000. In particular, these polymer molecules tend to coil at modest temperatures and uncoil at higher temperatures, to contribute the desired viscosity-temperature characteristics. It is, in fact, the coiling that prevents viscosity-improver-containing lubricants from thickening excessively at ordinary and low temperatures.

At the highest molecular weight, usually 10,000,000 or more, we find the additives that reduce the onset of turbulence, either for petroleum or aqueous applications. These polymer molecules are long enough to disrupt the formation of eddies and permit laminar flow at rates that would otherwise become turbulent.

In between, with molecular weights from about 400,000 to 4,000,000 (depending on which polymer), are the tackifiers and antimisting additives. The polymer in the first synthetic tackifiers was polyisobutylene of 1,000,000–2,000,000 molecular weight. More recently, polyisobutylenes of near 4,000,000 molecular weight have been used, as have olefin copolymers somewhat less than 500,000.

Polyisobutylene, when manufactured under suitable conditions, can be used in lubricants with incidental food contact [1], but ordinary petroleum oil may not be so used. A food-grade tackifier is made by dissolving polyisobutylene in a suitable technical white oil, and its properties are otherwise similar to the nonfood-grade product.

For environmental and renewable-resource reasons, lubricants and greases based on vegetable oils are appearing, especially for environmentally sensitive applications [2]. Tackifiers that are commonly used in petroleum oils are ineffective or even insoluble in these diluent oils. Tackifiers for these lubricants can be made from polymers or copolymers of dienes and styrene. While these may be less oxidatively and thermally stable than polyisobutylene, their useful range is sufficient to cover the intended conditions of use of the vegetable oil-based lubricants.

2 EARLY HISTORY OF TACKIFIERS

Tackifiers are among the first polymer-based additives used in lubricants; in 1934 Charles Kiemgard obtained a patent for grease tackified with natural rubber [3]. By 1942 John Zimmer and Arnold Morway had introduced polyisobutylene/acrylic crylic mixtures as an improvement over natural rubber [4]. Early citations in fluid lubricants include polyisobutylene in oil used for corrosion-resistant coatings [5] and for air-filter oils [6].

Tackifiers are solutions of polymers in oil, and through most of their history they were limited to polyisobutylene dissolved in petroleum oil. More recently, however, other polymers have been used to make petroleum oils tacky; tackifiers have been used for systems other than petroleum oil, and inhibition of misting has spun off as a new and potentially larger application.

2.1 Tackifier Manufacture

Generally, the tackifier market is too small to justify a plant devoted to the manufacture of a specific polymer. Tackifier polymers are therefore selected from the polymers commercialized for other uses and represent only a small percentage of the market for that polymer. The polymers are made according to well-established manufacturing techniques—cationic polymerization in solution for polyisobutylene [7]. Ziegler–Natta polymerization for ethylene-propylene polymers, etc. [8]. The Chemistry of the polymerization process is well documented in the synthetic rubber literature and will not be duplicated here.

The polymers used in tackifiers for petroleum-based lubricants are generally supplied in the form of “bales,” rectangular blocks of polymer of 55–75 lb (25–35 kg), wrapped in polyethylene film. The additive is made by mechanically grinding the polymer to 2–5-mm size and immediately dissolving in a light petroleum oil. The dissolving cannot be delayed; the small pieces would stick back together in minutes. A normal dissolving temperature is 200°F (90°C), and good agitation is required. After inspections, the tackifier additive is drummed through a filter.

2.2 Molecular Weight of Polymers

The polymers we are discussing usually do not have single molecular weights; each sample is a distribution over a range of molecular weight. A polymer chemist will refer to many different types of averages to describe the average molecular weight

of a commercial polymer [9]. These averages differ due to the weighting given in averaging the molecular-weight fractions. Some averages describe the statistics of averaging (number average, weight average, etc.), while some describe the analytical technique (viscosity average, etc.). In a product of narrow molecular-weight distribution, the averages will be close to one another. In a wide distribution, the averages will differ considerably. Regulatory matters are usually based on number average.

In this chapter, for example, the molecular of polyisobutylenes is the viscosity average, which is the one needed for specifying a commercial grade of polyisobutylene. However, the molecular weight of an olefin copolymer is instead a number average, which is the value one would relate to a commercial grade of olefin copolymer. When discussing properties of different polymer types, however, minor differences in molecular weight (less than a factor of 2) should not be taken too literally unless it is certain that the same type of average is being used.

For our purposes we will ignore these differences for the pragmatic reason that each chemical type usually employs a single method of reporting the average, and the type of average changes with different chemical types.

2.3 Testing of Tackiness

The time-honored “finger test” is still the easiest qualitative demonstration of tackiness. Unfortunately, no quantitative method is in widespread use. The “eggbeater” test is sometimes used as a tackiness demonstration. The oil is agitated with an actual eggbeater; a tacky fluid rapidly climbs the shaft. This behavior, known as the “Weissenberg effect,” is characteristic of viscoelastic liquids. Both the eggbeater and finger tests are really demonstrations rather than tests.

One sometimes-used test is the “ductless siphon”: a vacuum is drawn on a capillary under the liquid surface, and the liquid level is lowered so that the capillary is above the surface. The suction pulls tacky liquids up even through the airspace. Tackier solutions will draw a longer filament than will less tacky solutions; nontacky solutions are not drawn across the airspace at all. The height of filament that the vacuum will support is the test result. The easiest way to perform this test is to use a graduated cylinder as the container; the siphon draws the level down until the filament breaks. The ductless siphon differs from the other demonstrations in that it gives a numerical result, but this test is neither widely used nor has it been adopted by any standardization organization.

Tackifiers are also used as additives in lubricating grease. They are used not only to give grease a “stringy” consistency, but also to improve water resistance. Again, there is no test for tackiness beyond the fingertips. The water resistance is usually measured by the water sprayoff test, ASTM D 4049 [10], which has generally replaced the older water washout test, ASTM D 1264 [11].

2.4 Shear Stability

As organic molecules go, the polyisobutylenes used in tackifiers are really large. In a 1.5-million molecular-weight polyisobutylene for example, the chain is composed of almost 30,000 monomer units, each monomer unit contributing almost 2.5 Angstrom units to the chain length. Since polyisobutylene chains are essentially fully extended in solution [12], the average molecule is several micrometers long! That's only the average length; many molecules are considerably longer. A micrometer is

not a short distance in lubrication technology; pores in filters are frequently only a few micrometers in diameter, and clearances in control valves can actually be sub-micrometer. In boundary lubrication and elasto-hydrodynamic lubrication conditions, one micrometer is comparable to the lubricant film thickness.

The two ends of a polymer chain are not necessarily, therefore, in the same flow environment. In particular, one end of the chain can be in one flow situation and the other end can be in a section of fluid moving away from the first end. Macroscopic tension on a polymer chain can break it and consequently cause loss of thickening and tackiness. All tackifiers, therefore, are subject to breakdown by shear, and the most important governor of breakdown is the starting molecular weight.

Various experiments have tried to objectively evaluate shear stability of tackifiers by measuring viscosity loss after shear, but have not succeeded. Each tackifier sample contains molecules of a broad range of molecular weight, and the highest molecular-weight fractions are the most subject to shear breakdown. The thickening contribution increases with the molecular weight, but the tackifying contribution increases more steeply. Shear, therefore, causes a loss of tack and a drop in thickening, but the tackiness can be lost before much thickening loss is observed. The important lesson is that viscosity loss cannot be used as a quantitative surrogate for tackiness in evaluating shear stability.

Even a tackiness demonstration like the finger test may be useful in comparing shear stability of tackifiers. One tackifier may become nontacky in the finger test after one pass through a homogenizer, for example, while another tackifier might require three or four passes. The second is obviously the more shear stable.

In greases, the shear stability is normally evaluated by one of the mechanical stability tests, such as the change in penetration after 10,000 strokes in a grease worker, or after the roll test, ASTM D 1831 [13]. Again, evaluate tackiness subjectively, separate from any change in penetration.

2.5 Thermal Stability

For tackiness, the polymer chain should be as fully extended as possible. One property that causes chain extension is steric hindrance between monomer segments. Generally, this steric hindrance requires that the monomer be 1,1-disubstituted, as isobutylene is.

Polymers of 1,1-disubstituted monomers, however, tend to be thermally unstable. Unlike other polymers, which do not exist in equilibrium with their monomers, these exhibit a “ceiling” temperature, a temperature where the polymer and monomer can exist in equilibrium [14]. At higher temperatures the polymer simply depolymerizes. In practice, these polymers are not commercially useful as high as their ceiling temperature; the evaporation of monomer drives the equilibrium toward depolymerization at lower than the ceiling temperature. A technical data sheet [15] on a polyisobutylene-based tackifier warns that “Viscosity stability is lost at temperatures in excess of 92°C,” which is a temperature well within the parameter of the manufacturing process, for example, of certain greases.

Olefin copolymer-based tackifiers, however, lack the 1,1 substitution pattern and are, therefore, as thermally stable as, for example, the diluent oil.

Thermal stability is not normally a problem with the polymers used as antimisting additives in soluble metal-working oils or synthetic coolants, due to the volatility of water limiting the temperature.

2.6 Antimisting

Tackifiers have long been used as aids to coalescence in mist-lubricated pneumatic systems, such as “rock-drill” oils. Misting oils are also used to continuously lubricate bearings etc. For these applications, some misting must be allowed even as the additive enhances coalescence. But a newer concern has made the misting of lubricants newsworthy—the unintentional misting of metal-working lubricants and coolants, and the inhalation hazard of the mists.

The process of creating small drops or aerosols is well known from the technology of intentionally created mists: mechanical energy breaks a fluid into a thin sheet, which then breaks into filaments, which then break into droplets. For a Newtonian fluid these breaking processes depend on many fluid variables, including the viscosity, surface tension, and density, as well as the mechanical variables. While the breakup of such a viscous jet has been well studied, the mathematics of the breakup of a viscoelastic jet has not been reported in the literature.

One can imagine, however, an element of fluid that somehow disengages from the main fluid body, whether intentionally from a mist-generating device like a sprayer, or unintentionally from contact of the fluid with a high-speed mechanical part, such as in a grinder or mill. As different parts of the fluid element are moving, in general, at different velocities, the element becomes elongated to a filament. If this process continued indefinitely, the diameter of the filament would become too small to sustain its integrity, and the surface forces would break the fluid into droplets, giving a mist.

With a tacky fluid, however, the extension of the filament is inhibited by a tensile force. The tensile force inhibits the extension to the breakup point, the filament contracts back to a relatively large drop, and there is no misting.

While the underlying theory is only qualitative, the effect is easy to demonstrate: if you spray a Newtonian fluid from a manual aerosol nozzle, the fluid forms a mist (which is, after all, the intent of the spray nozzle). But if you spray a viscoelastic fluid such as a fluid with an antimisting additive, you get a single stream. There is one disadvantage to using tackifiers in “straight” cutting oils—the tackifier increases the “dragout” of cutting oil on the parts and chips, thereby increasing the consumption of cutting oil. Antimisting additives are available, however, that are the same polymers used in tackifiers but lower in molecular weight. These inhibit misting without excessive increase in dragout.

To inhibit misting, the polymer must be in its extended configuration. In a two-phase system, a minimum requirement for getting the polymer into its extended configuration is that it be in the continuous phase rather than in the dispersed phase. Conventional oil-soluble tackifier polymers, therefore, are effective inhibitors of the misting of “straight” oils (oil-diluted metal-working fluids) but are ineffective in “soluble” oils (emulsions of petroleum fluids in water) and “synthetic” (oil-free) coolants; these applications require a water-soluble polymer. Three categories of water-soluble polymers have been tried: polyalkylene glycols, ionomers, and

proprietary emulsions. There are also natural products, proteins, and carbohydrates that are water-soluble and of high molecular weight. These are generally considered good food for bacterial growth and are, therefore, not used.

The major problem with solid water-soluble polymers such as polyalkylene glycols is the dissolving process; the wet polymer particles form a nearly impenetrable and very viscous coating, making further dissolution impractical. The alternative is to dissolve the polymer in a separate container, using a properly equipped high-speed mixer. The product is a viscous liquid additive that contains little polymer and therefore needs to be used at a high treatment level of more than 1%. Dissolution in metal-working coolants can still be complicated, and the low polymer level in the additive can make the treatment costs prohibitive.

Ionomers are acrylic acid copolymers. Under slightly acidic conditions, the polymer chain is coiled and the solution's viscosity is modest. Dissolved in an alkaline metal-working coolant, the polymer's acid groups are converted to their anion form, repelling one another and causing the molecular chain to fully extend. While this could, in principle, provide a tractable antimisting additive, the difficulty is that the available ionomer polymers are too high in molecular weight and the shear stability is very poor. Also, a pH adjustment would be needed after tankside addition.

The proprietary emulsions are emulsions of water-soluble polymers in a petroleum diluent. They are, therefore, low viscosity and easy to handle despite having a relatively high concentration of high-molecular-weight polymer. When added to water, these emulsions invert so that the polymer is now in the water phase of the coolant. After an interval to allow full chain extension (a minute or two is sufficient), these additives give good misting inhibition at treatment levels below 0.05%. These products were new introductions in 1999, but are expected to become a significant factor in protection against metal-working mists.

Shear will eventually consume any antimisting additive, and tankside replenishment will be necessary even when the starting coolant is mist-inhibited.

Metal-working antimisting additives compete with other mist-control technologies, specifically mist-collecting ventilation systems. While these systems are very costly and restrict access by the operator, once they are in place they limit the environmental benefits in using antimisting additives. Ventilation systems do require filters, however, and replacement filters may cost a large shop tens of thousands of dollars annually plus installation costs. In such shops, the additives might be justified by the reduction of filter replacement costs.

2.7 Testing of Antimisting Properties

Due to concerns regarding inhalable metal-working fluid mists in the workplace, OSHA has established air-sampling methods to measure inhalable mists. One demonstration of antimisting effectiveness, therefore, is to measure the mists with and without the additive.

The difficulty with the air-sampling tests, however, is that they focus only on the small particles, specifically those below 0.5 micrometers. The limitation stems both from the difficulty in sampling larger particles accurately and from the concern with particles that are too small to be seen. In a shop that creates a visible mist, however, the additive can cause a visually clean workplace while reducing the air-sampling measurement by as little as 25%. OSHA has apparently focused on the

particles that are not visible since the visual comparison is sufficient for the larger visible mists. It would be foolish to believe that the inhalation of these larger particles does not have hygienic effects similar to the smaller particles. Air-sampling tests therefore understate the value of antimisting additives.

Reduction of gross misting is easily demonstrated with a hand-operated spray nozzle, which is commonly found in a housewares department of a grocery store.

In a machining environment, the variation among metal-working machines and operating conditions is so great that there is really no substitute for a field trial. The field trial should be of a sufficient duration to evaluate the need for tankside additions in service.

3 THE FUTURE

We will see the development of a recognized method for measuring the tackiness of tacky fluid lubricants. While tackifiers will continue to be used to make greases stringy, nontackifier polymers specifically aimed at water resistance will replace tackifiers for this purpose.

Antimisting additives will be widely used in soluble oils and semisynthetics as tankside additives, and in synthetic coolants both as tankside additives and as components of synthetic coolant concentrates.

REFERENCES

1. FDA regulation 21, CFR 178.3570.
2. Presidential order 13101, Sept. 1998.
3. U.S. Patent 1,979,943 (1934).
4. U.S. Patent 2,275,123 (1942).
5. U.S. Patent 2,453,833 (1944).
6. U.S. Patent 2,732,356 (1952).
7. RM Thomas et al. *J Am Chem Soc* 62:276, 1940.
8. S Boot. *Ziegler-Natta Catalysts and Polymerization*. New York: Academic Press, 1979.
9. FW Billmeyer. *Textbook of Polymer Science*. New York: Interscience, 1962, p 6.
10. ASTM Book of Standards, vol. 5.02, 1999.
11. ASTM Book of Standards, vol. 5.01, 1999.
12. ASTM Book of Standards, vol. 5.01, 1999.
13. P Flory. *Principles of Polymer Chemistry*. Ithaca, NY: Cornell University Press, 1967, p 246.
14. KJ Ivin. In J Brandrup, EH Immergut, eds. *Polymer Handbook*. New York: Interscience, 1967, pp II-389-395.
15. Exxon Chemical Company technical data sheet for Paratac.

Seal Swell Additives

JERRY K. SIERON

Universal Technology Corporation, Dayton, Ohio, U.S.A.

RONALD E. ZIELINSKI

PolyMod® Technologies, Inc. Fort Wayne, Indiana, U.S.A.

1 INTRODUCTION

The use of additives in lubricants, both military and civilian, began around 1930. Prior to that time, additives in lubricants were not required since most fluid systems operated at low-pressure and low cycling rates. Certainly, seal swelling agents were not required since seals were generally made from leather or similar materials not subject to swelling by the petroleum-based fluids in use at that time. The use of additives to improve fluid performance began with the military fluids. Industrial fluid development paralleled or followed the military fluid development.

With the enhanced development of military aircraft and reciprocating engines spurred by World War II starting in approximately 1935, advanced fighters and bombers required new, high-performance lubricating fluids and seals. The new military fluids were based largely on petroleum base stocks or mineral oils for hydraulic systems. These consisted of paraffinic, aromatic, and alicyclic (naphthenic) components. Various additives including rust inhibitors, oxidation inhibitors, detergents/dispersants, viscosity index improvers (VI), pour point depressants, antiwear components, and antifoam materials were used to develop additive packages for these hydraulic fluids depending on aircraft type and intended missions. These development efforts resulted in the creation of a military specification—MIL-H-5606—for these fluids. The specification allowed for some flexibility in formulation for competitive purposes and guaranteed a performance band for the fluid and its compatibility with elastomer seals.

Similarly, new reciprocating engine lubricants based primarily on diesters of both aromatic and aliphatic acids plus additive packages for fluids intended for each aircraft engine type, i.e., high-flying bombers (B-17s) and fighters (P-47s), were developed. These were the early versions of MIL-L-7808.

High-acrylonitrile-content butadiene-acrylonitrile (NBR) seals were used for these aircraft hydraulics and worked fine except when strategic aircraft flew for long time periods at very high altitudes (i.e., >30,000 ft): the seals leaked, thus the base polymer had to be modified with a lower acrylonitrile content to improve low-temperature performance. Of course, seals made from NBR with reduced acrylonitrile content have higher butadiene content and thus would have increased volume swell in petroleum-based fluids. This caused many problems. Programs driven by the military had material and chemical engineers working together and adjusting both fluid and seal formulations to solve the problems. The results of these coordinated efforts were the development of fluids and seals that were complementary.

It is very difficult to speak in specific terms with regards to seal swell additives, since commercial fluids have additive packages, which are considered very proprietary and highly confidential. In order to address seal swell additives, we will follow the development of military fluids and seals in three basic timeframes: 1935–1960, 1961–1980, and 1981–2000. In general, specific information of compositions of most aircraft fluids, including seal swell additives, is extremely limited and is usually, again, company confidential. However, because these developments were, at least, in part supported by the military, more information is available. We describe what is known about swelling agents, yet recognize that generalities will have to suffice due to the confidential/proprietary nature of formulated fluids. Industrial fluid development, including seal swell additives, followed the military fluid development and the additives used in military fluids were used in the industrial fluids so, in essence, by following the military fluids we are also following the industrial fluids since both used essentially the same seal swell additives.

2 FLUID/SEAL SWELL ADDITIVES DURING 1935–1960

During this period, petroleum-based fluids predominated as the fluid of choice for hydraulic fluids. The earliest versions of the military fluid designated MIL-H-5606 (mineral oil) had a higher aromatic content and thus provided sufficient volume swell for the high-acrylonitrile (ACN) NBR (nitrile) seals used in the low-pressure (~ 1500 psi) hydraulic systems in piston engine aircraft. As aircraft development proceeded, more powerful piston engines were developed for the very long-range bomber missions, primarily the B-17, to be used by the Army and Air force for attacks on enemies in Europe and the Far East theaters. The long-range bombers flying at very high altitudes, 35,000–45,000 ft, caused oil thickening and seal leakage resulting in sluggish performance. The seals used were nitrile seals designated by the military as MIL-R-25732. Fighter aircraft, both land-based and aircraft carrier-based, did not experience problems because they flew at lower altitudes and for shorter missions. To solve the bomber fluid problem, the mineral oil base fluid was further refined to replace some aromatic content with aliphatic content to improve low-temperature viscosity at –65°F. This resulted in a revised version of MIL-H-5606 hydraulic fluid. Low-temperature sealing performance of the high-ACN NBR-content MIL-R-25732 seals was improved by replacing some of the high

ACN NBR with medium or low ACN NBR as the base polymer and/or replacing part of di-2-ethylhexylphthalate (DOP) processing oil used in seal compounding formulations with di-2-ethylhexylsebacate (DOS) oil. Fluid formulators added sufficient diester fluid, such as DOS, to the MIL-H-5606 to maintain 18–30% seal volume swell. Although very early piston engines used petroleum-based oils as lubricants, this gave way to pentaerythritol ester-based fluids to improve low-temperature performance to -65°F and maintain high-temperature performance at 275°F . MIL-R-25732 seals were used for engine lube sealing. For naval aircraft, antirust additives were added to fluid formulations for obvious reasons.

Commercial aircraft versions of military aircraft during this era were developed, i.e., Douglas DC-3 (C-47 military transport), Douglas DC-6, and Lockheed Constellation. These aircraft initially used military aircraft hydraulic oils/seals and engine lubrication oils/seals. However, because of the short flight duration and many takeoffs and landings of these aircraft, a new, more fire-resistant fluid was introduced. These new fluids had a phosphate ester base stock, which created the need for seals made with a polymer compatible with this new base stock.

3 FLUID/SEAL SWELL ADDITIVES DURING 1961-1980

As advanced military aircraft with enhanced performance (jet aircraft) and missions were developed, both hydraulic system and engine operating temperatures increased. Oil companies and seal manufacturers responded by enhanced synthetic oil development and corresponding seal development to meet aircraft and gas turbine engine manufacturers needs for -65 – 350°F performance. Oil companies synthesized thermally stable polyalphaolefin (PAO) fluids to meet the desired 350°F high-temperature fluid requirement; this was formulated with various additives such as antioxidants, lubricity additives, antiforms, metal deactivators, rust inhibitors, viscosity index improvers, and seal swell materials to meet 18–30% volume swell. The first synthetic military hydraulic fluid developed was less flammable than MIL-H-5606 and was designated as MIL-H-83282. MIL-H-83282 had an operational range of -40 – 350°F . Seals based on sulfur-donor or peroxide-cured NBR were developed for this fluid. The new seals were designated as MIL-R-8346 1 and were developed to meet the -65 – 350°F operational requirements.

The MIL-H-83282 fluid contained a significant amount of diesters to achieve desired seal volume swell. This fluid found almost immediate use in most military aircraft, except for the Air Force strategic aircraft; for example, the B-52, B-tB, KC-135, and KC-10, which required good -65°F viscosity, did not use this fluid, which became very viscous below -40°F . This shortcoming was later resolved by the development of a PAO (polyalphaolefin) based fluid designated MIL-H-87257, which is currently being implemented. This low-temperature PAO fluid was achieved by synthesis of lower-molecular-weight PAOs and replacing part of the higher-molecular-weight fractions present in MIL-H-83282. This approach caused a small loss in nonflammability capability but met the desired capability of a universal less-flammable hydraulic fluid for all military aircraft and with a -65 – 350°F range capability.

During this timeframe, engine lubrication fluid requirements were also increased to -65°F to 350°F , which led to the development of diesters of both adipic and sebacic acids, especially dioctyladipate (DOA) and DOS, with the latter predominating. These were formulated to later versions of MIL-L-7808 for both military

and commercial aircraft. During this time, seals were also formulated with fluorocarbon polymers to meet a -40 – 350°F operational requirement for these fluids. These seals were designated by the military specification MIL-R-83485. Seal swelling additives were not needed for the MIL-L-7808 lubrication fluids, since both NBR and fluorocarbon (FKM) seals exhibit swelling in these fluids.

During this 1961 to 1980 timeframe, commercial aircraft were now using the nonflammable phosphate ester fluids. Ethylene-propylene-(EPM) or ethylenepropylene diene-(EPDM) based elastomeric seals were developed for these fluids. Since the phosphate ester base stock acts as a plasticizer, there was no need for seal swell additives in these fluids.

4 FLUID/SEAL SWELL ADDITIVES DURING 1981–2000

As mentioned previously, MIL-H-83282, a polyalphaolefin (PAO) based hydraulic fluid, was developed during the late 1960s and during 1970s, with implementations in most nonstrategic military (i.e., F-16, F-14, F-18 fighters) aircraft beginning in the late 1970s after extensive flight testing. The Air Force's strategic aircraft—long-range/high-altitude bombers, tankers, and reconnaissance aircraft—continued inued to use MIL-H-5606 to accommodate its need for a hydraulic fluid with a -65 – 275°F capability. The desire for a less flammable fluid with better low-temperature viscosity led to the development of MIL-H-87257. This fluid balance the PAO content with the proper molecular-weight range of PAO components. With the proper additive package, including sufficient quantities of diesters (i.e., DOS) to achieve seal swell of 18–30%, dynamic cycling testing indicated this new fluid had the desired capability of -65 – 350°F as well as compatibility with both MIL-R-83485 (fluorocarbon) and MIL-R-83461 (NBR) seals. All military aircraft, including strategic aircraft, are currently conducting flight testing. It appears likely that MIL-H-87257 could eventually be the universal hydraulic fluid (-65 – 350°F) for military aircraft.

During this time, commercial aircraft continued to use phosphate ester fluids for hydraulics with the previously mentioned EPM/EPDM based seals. Engine lubrication fluids are still primarily the DOS, MIL-L-7808, type fluids for both military and commercial jet aircraft. Seal swelling materials are not required since the diester fluids accomplish this purpose.

5 TRENDS AND THE FUTURE

It is very likely that advanced military fighter aircraft, namely the F-22, JSF (Joint Strike Fighter), and the latest model F-18, will have the requirement of hydraulic fluid with a -65 – 350°F capability or, more likely, a -40 – 350°F capability with a pressure of 4000 psi. MIL-H-83282 would meet these requirements for the F-22 and the Air Force version of the JSF. This fluid would also meet Navy fluid requirements for its advanced F-18 and Navy's version of the JSF. Currently, seals for these systems would be MIL-P-83461 NBR, and/or the higher-temperature capability MIL-R-83485 fluorocarbon materials. Newer polymers are also investigated as potential seal materials for these systems since nitrile elastomers oxidize when exposed to temperatures above 250°F for extended periods of time, and fluorocarbon elastomers cannot achieve the low-temperature requirement of -65°F . The Air Force and Navy will build these aircraft over a 10–20-year period, with several

models available for domestic, partner countries, and foreign military sales. Strategic aircraft needs over the next 20 years will likely be met by the C-17 transport; KC-10 or a tanker version of the C-17 (a KC-17); while strategic bomber needs are likely to be met by the B-1B, B-2, and an advanced version of the B-2 stealth aircraft. While there could be some changing needs in both hydraulic and engine lubrication fluid needs, it is currently not possible to determine specific fluid/seal needs or seal swelling agent needs.

Commercial aircraft requirements over the next 20 to 30 years are not likely to involve major changes. Airframe designs and engine requirements will not change substantially but will likely feature incremental improvements in performance and, as always, be dependent on customer requirements. Therefore, a dramatic change is not expected in hydraulic or lubrication fluid/seal needs for commercial aircraft.

6 INDUSTRIAL FLUIDS

As stated earlier, industrial fluid development has closely followed the development of military fluids. Natural base oils including mineral oils have been used in industrial fluids. These fluids are not as controlled as military fluids, which have developed specifications to meet and essentially perform the same within a narrow band of additive variability, allowed by the specification for competitive bid requirements. Industrial fluids vary widely as a result of their crude source, e.g., whether paraffinic, naphthenic, mixed, paraffinic-naphthenic, and the like; as well as their formation, e.g., distillation range, straight run or cracked, hydrotreated, solvent extracted, and the like. Because these fluids vary widely, the additive packages are very proprietary, but again the seal swell additives parallel those used in military fluids.

DOS and DOP are used in industrial fluids. Other seal swell additives include mineral oils with aliphatic alcohols such as tridecyl alcohol. Oil-soluble, saturated, aliphatic, or aromatic hydrocarbon esters such as dihexylphthalate are very popular. Trisphosphite ester in combination with a hydrocarbonyl-substituted phenol is also used as a seal swell additive. As more highly refined mineral oils and synthetics based upon PAO enter the market, it is not likely that there will be significant differences in seal swell additives.

7 SEAL SWELL DILEMMA

When a fluid is formulated, the usual concentration of seal swell additive is 0.6–1.0% by volume. During development, the fluid manufacturer uses standard test elastomers to determine fluid seal swell, which is normally targeted at 18–30%. These tests are normally 70 to 168 hr in duration and do not allow for a full measure of fluid/seal compatibility evaluation. The fluid is then marketed as compatible with the elastomer seal. The dilemma is that the seal used in the actual system is much different than the elastomer used for seal swell determination, and swell beyond 20% is normally not allowed by elastomer specification or desired from a performance standpoint. Thus, we have fluid, developed to produce high seal swell, and an elastomer seal that is not allowed to swell beyond 20%. This dilemma occurs because fluid and seal development are no longer coordinated. In the past with the military driving parallel development programs, fluids and seals were simultaneously developed; this is not true in today's commercial arena. The fluid

manufacturer has been taught that high seal swell is good. It allows for more seal force and less compression set. The problem is that seals that swell excessively soften and completely fill the seal gland. These conditions for dynamic seals lead to nibbling of the seal as it overflows the gland and to excessive seal wear. This leads to premature seal failure and leakage, which results in costly down time while seals are replaced.

To put fluid developers on the same track as seal developers, ASTM Committee D 02 has developed ASTM D 6546. This specification details a fluid—elastomer seal test program, which involves the testing of commercially available elastomers in the new fluid at actual service temperatures for long periods of time (1000 hr). These test conditions with recommended limits allow for a more complete evaluation of fluid-seal compatibility and should allow for optimized fluid formulations with a minimum amount of seal swell additive.

8 COST-EFFECTIVENESS

It is important to minimize the amount of seal swell additive in fluid formulations. Seal swell additives increase the cost of mineral- and PAO-based hydraulic fluids. This is because the rather large amounts of di-2-ethylhexylsebacate (known commonly as DOS) is expensive when compared to the cost of the base stocks, but it accomplishes the purpose of seal swell. It must be remembered that qualification testing of fluids and seals, not to mention quality-control testing of both, is inherently expensive. This is why the implementation of ASTM D 6546 should be a cost-effective, integral part of the fluid development process. The fluid developer can also use the results of his or her tests to instill confidence in the fluid users that they are provided with a fluid and recommendations for seals substantiated by long-term testing.

The long-term testing can also provide useful information to the fluid user, which can help plan preventative maintenance programs, which would avoid or minimize costly down time. Fluid stability tests are already performed for 1000 hr; these additional tests would be extremely cost-effective in optimizing the fluid formulation and addressing total system needs—fluid and seals.

9 MANUFACTURING

Manufacturing of both fluids and seals is an extremely competitive and very proprietary business. This has not changed over the years and is not likely to change in the foreseeable future. In general the following is true: (1) the competitive nature of the two business types has controlled product costs; (2) the fluids with the reputation for long life with a minimum of problems are the most successful. Fluid formulation plans that include testing to ASTM D 6546 or similar specifications can be very cost-effective over the long run since fluids would be developed with optimum concentrations of expensive additives, and long service life with compatible seals would be demonstrated.

10 SUMMARY

Seal swell additives are necessary in many fluid formulations. Seal swell can be beneficial in slowing compression set. However, excessive seal swell can be deleterious to

seal life and system performance. Seal swell additives add cost to the final fluid formulation, so minimizing the concentration of these additives is important from a financial standpoint. For both the fluid and seal developer, ASTM D 6546 represents a method to ensure that the seal and the fluid with its additive package are fully compatible. Whatever the proprietary formulation is, the fluid, developer can demonstrate seal compatibility with confidence over a long period of time. He or she can also tailor the amount of seal swell additive for maximum seal performance and minimum cost.

Biocides as Lubricant Additives

WILLIAM R. SCHWINGEL

The Dow Chemical Company, Buffalo Grove, Illinois, U.S.A.

1 INTRODUCTION

Metal-working fluids provide a number of functional properties vital to metal-working operations. Designed as a coolant and lubricant and to provide corrosion resistance, electrochemical resistance, extended resistance to microbial degradation, and biodegradability in the environment, metal-working fluids must also be safe for human use and exposure. The failure of a fluid to perform any one of these demands has the potential to result in operational complications, process shutdowns, and product-quality issues. Perhaps one of the most common and controllable complications is microbial degradation. All metal-working fluids contain the nutrients necessary to sustain microbial growth, including mineral base stocks, glycols, fatty acid soaps, amines, sulphonates, and other organic components. Emulsifiable, semi-synthetic, and synthetic fluids and fluids concentrates (containing water), however, are especially vulnerable because they contain water, an important requirement and a notorious source of microbiological contamination. Conversely, neat oils, while not immune to contamination problems, show greater overall resistance to microbial degradation simply because they do not contain water. To ensure optimum, long-term performance of any fluid, protection against microbial degradation should be an integral part of the metal-working process.

2 MICROBIOLOGICAL GROWTH

The two types of microorganisms that contaminate metal-working fluids, bacteria and fungi, frequently occur independently in a fluid, but they can also coexist. The types of organisms present, and their ability to coexist in the same fluid, depend on fluid composition and environmental conditions.

This chapter is property of The Dow Chemical Company, a corporation organized and existing under the laws of the State of Delaware, United States of America, with business offices located in the city of Midland, Michigan. United States of America.

2.1 Bacteria

Bacteria—single-cell organisms that lack the internal cell organelles found in higher forms of life—are classified as either Gram-positive or Gram-negative depending on their cell wall structure, and as aerobic or anaerobic according to their requirement for oxygen. Anaerobic bacteria cannot grow in the presence of oxygen; however, strict anaerobes can tolerate very short exposure to oxygen before dying. Another group of bacteria, facultative anaerobes, is able to use metabolic pathways like those of aerobes when oxygen is present and then switch to anaerobic metabolism when oxygen becomes limited. The compounds produced from anaerobic pathways create the unpleasant odors associated with the degradation of fluid quality and performance. The compounds produced through anaerobic pathways may include organic acids, as well as poisonous and explosive gases such as H_2S and H_2 .

Not all bacteria are able to survive in the aqueous environment of metal-working fluids, and their occurrence is often specific to certain formulations. However, *Pseudomonas aeruginosa*, *Enterobacter cloacae*, *Escherichia coli*, *Klebsiella pneumoniae*, and *Desulfovibrio* spp. are commonly found in all types of fluid. Because these bacteria are the species most predominantly found in rivers, streams, lakes, and soil, it follows that makeup water is viewed as a significant source of bacterial contamination. Other contamination sources include air, raw materials, and animals, including humans. When bacteria are present, they are generally distributed throughout the metal-working system and multiply rapidly when conditions are favorable.

2.2 Fungi

Fungi may occur as either yeasts or molds. Yeasts, like bacteria, are unicellular and usually spherical in shape. Conversely, molds are composed of more than one cell and form complex mazes of filamentous hyphae with spore-bearing structures that give them their powdery, matlike appearance. They are widespread in the environment and are commonly seen on decaying foods such as bread, fruit, and cheese. Fungi are often found in metal-working fluids but are usually found in lower concentrations and distributed less evenly than bacteria. Fungi tend to grow on solid surfaces such as splash areas and in sluices, troughs, filters, and pipes. Although many different species of fungi have been isolated from metal-working fluids, *Fusarium* sp., *Candida* sp., and *Cephalosporium* sp. occur most frequently.

2.3 Biofilms

Although microorganisms can exist in the free-flowing metal-working fluids in central systems, a large proportion of the microbial population exists within biofilms. Often composed of diverse populations of microorganisms and complex in structure, biofilms adhere to system surfaces. Both chemical and biological material can become trapped in the secretions of a biofilm's living cells. Biofilms can vary in thickness but usually range from a few millimeters to several centimeters. The environment within the biofilm is highly influenced by the microorganisms present and may be very different from the conditions in the fluid itself. Because the microorganisms growing within a biofilm are protected from the conditions that may be affecting the bulk fluid, the ability of chemical microbiological agents to effectively

control their growth is limited. This explains why chemical control treatments shown to be effective in laboratory testing sometimes fail in field situations.

3 A MICROBE-FRIENDLY ENVIRONMENT

The primary factors affecting microbial growth are the availability of water and nutrients, system pH and temperature, and the presence of inhibitory chemicals. With the introduction of water as an important component of metal-working fluids, microbial growth has become a major concern. Like all living organisms, bacteria and fungi require water for survival, which is present in all emulsifiable, semisynthetic, and synthetic metal-working fluids. In regard to nutrients, metal-working fluids are capable of providing all the essential nutrients needed to support microbial growth [1]. These include carbon, nitrogen, phosphorus, sulfur, and other trace elements. Small quantities of inorganic salts are also crucial for microbiological growth, which means variances in water hardness can influence microbial survival. And, while at least some level of inorganic salts must be present, very high salt concentrations may actually inhibit growth.

In regard to pH, the ideal level for optimum bacterial growth is a neutral or slightly acidic pH of 6.5–7.5. Fungi prefer a slightly lower pH of about 4.5–5.0. However, both bacteria and fungi can survive in fluids with pH levels outside these ranges. A large contingent of microorganisms thrives in typical metal-working fluid pH ranges; however, species diversity decreases in fluids with pH levels of 8.5 and higher.

The optimum temperature range for mesophiles, the largest contingent of microorganisms, is 30–35°C, the temperature range of most metal-working fluid systems. However, many organisms can exist at extreme temperatures; for example, bacteria have been found growing in both Arctic climates and at the mouths of geysers and hot springs.

By manipulating these various growth factors, microbial survival and expansion can be controlled and even prevented. Water quality and pH are the two factors most easily managed. However, the availability of nutrients can be regulated through the strategic selection of raw materials that are inherently more resistant to microbial degradation. Components such as borates, certain amines, and biocides can all inhibit microbial growth. While little can be done to control fluid temperature, factors such as oxygen availability can, if not slow microbial growth, at least alter microbial populations. For instance, a shift from aerobic bacteria to facultative or obligate anaerobe populations is likely to occur if metal-working fluids are not aerated or circulated.

4 DESIGN, MAINTAIN, AND MONITOR

In the ongoing quest for microbial control in metal-working fluids, system design, proper housekeeping, fluid maintenance, and microbiological monitoring programs all play an essential role. Microorganisms are less able to establish healthy populations in areas of high, uniform flow, so a well-designed system, one that eliminates or minimizes dead legs and stagnant zones, is ideal. For example, anaerobic bacteria are particularly likely to establish populations where flow is minimal, since this often limits the diffusion of O₂ into the fluid.

Good, consistent housekeeping practices at metal-working fluid end-use sites can significantly reduce the occurrence and proliferation of microbes. By preventing

contaminants from entering the system, good housekeeping practices reduce the amount of chemical and human effort needed to maintain a system. An all too common scenario occurs when metal-working fluid splashes around machines. These small puddles of fluid can harbor concentrations of 10^8 to 10^9 microbes/ml. When debris or built-up material is washed off or falls into central sumps, an extremely high microbiological burden is placed on the metal-working fluid's preservation package. Therefore, machine surfaces and work areas should be kept clean and free of debris or residue buildup. Operators should not rinse or sweep debris into return sluices, as this can inoculate central systems with contaminated material. Tramp oil is another significant source of contamination that should be removed. High levels of tramp oil are associated with microbiological preservation problems in metal-working fluids and are known to reduce the efficacy of chemical biological control agents [2].

Good housekeeping practices also require that workers wear clothing that is cleaned and kept on-site. This reduces the risk of workers' introducing contaminants such as dirt into the plant and transporting contaminants and other possible chemical and biological irritants into their homes. Food and human waste should also be prohibited from entering central systems, as they are both significant sources of contamination.

5 COMPLICATIONS AND CHALLENGES

Uncontrolled microbiological growth can significantly impact both the performance of metal-working fluids and the operation of the central system. The poor fluid quality and performance that microbial degradation causes can result in corrosion of machines, tools, and workpieces; loss of lubricity and fluid stability; and the formation of slime, which can plug filters and delivery lines and cause unacceptable odors. Microbial growth may also contribute to skin irritation and respiratory problems.

Fluid deterioration can be defined as any change that adversely affects a fluid's utility. Direct deterioration of metal-working fluids can be caused by a variety of microorganisms with the capability to degrade a number of the organic compounds that make up the intricate formulation of a metal-working fluid [3,4]. While components such as hydrocarbons, petroleum sulfonates, fatty acids, and fatty acid esters often remain unaffected by any one singular group of organisms, they are susceptible to attack from combinations of organisms. The degradation of these fluid components is responsible for loss of fluid performance; lubricity in particular is related to hydrocarbon degradation. Resourceful groups of microorganisms may even develop the ability to attack and degrade biocides, especially if they are used at sub-optimum levels.

Microbial contamination is also an indirect source of problems in fluid applications, including the generation of odors. The odors produced are associated with organic acids (primarily acetate, propionate, and butyrate) and hydrogen sulfide, byproducts of microbial metabolism. These compounds are formed when oxygen levels drop, allowing anaerobic bacteria to proliferate. A complication of weekend shut downs occurs when fluids are not circulated, causing fluid oxygen levels to drop; odors generated by this means are often referred to as "Monday morning odor." The odor often becomes so offensive that employees refuse to work until it is resolved.

Another complication of microbial contamination is a decrease in fluid pH. The organic acids generated from microbial metabolism have the potential to decrease

the pH of the fluid, and a fluid with a lower pH can be corrosive to ferrous materials. A decrease in pH also can result in emulsion splitting and decreased efficacy of other fluid components, including antimicrobial agents or biocides. To maintain proper performance, the alkalinity of the fluid must be boosted to the desired pH.

Microorganisms also can have a direct effect on corrosion through a process known as microbially influenced corrosion (MIC). Here, certain bacterial populations either establish an electrolytic cell or stimulate anodic or cathodic reactions on metal surfaces. This can cause pitting and corrosion on both machining tools and workpieces. Microorganisms can also degrade corrosion inhibitors, leaving metals more vulnerable to corrosion.

The formation of biofilm is a source of significant problems within the central system. Biofilm growth on machine surfaces can affect the heat-exchange characteristics of the system. If it sloughs off, it can interfere with mechanical operations such as fluid flow and filtration. Fungal contamination in particular plays a major role in the clogging of lines and filters. Considerable time and effort are required to remove biofilm from the system and resume efficient operations.

While health and safety are not the focal point of the material presented here, a few important points should be addressed. It is unreasonable to expect that any system can be kept entirely free from microbial growth; rather the goal should be keeping growth under control. If this is accomplished, health and safety concerns should not be an issue.

In general, microorganisms capable of surviving in metal-working fluids do not harm humans who come in contact with the fluids [5]. Pathogenic bacteria such as *Legionella* sp. need very nutrient-rich and controlled conditions for growth. In most cases, however, these human health conditions have resulted from improperly or poorly maintained metal-working fluid systems [6]. Thankfully, these conditions are not usually found in metal-working fluids, especially fresh use-diluted fluids. And, while it is very rare for healthy persons to contract diseases from the microorganisms found in metal-working fluids, anyone with a compromised immune system, or who is taking immunosuppressant drugs for any reason, will be more susceptible to microorganisms. Heavy microbial contamination, however, is a concern in regard to dermatitis and skin irritation.

It is suspected that certain bacteria may indirectly impact human health conditions, specifically Gram-negative bacteria that are common in fluids. The endotoxins present in the outer cell membrane of Gram-negative bacteria have been identified as a possible cause of pulmonary diseases and allergic reactions. Endotoxins have been found in relatively high levels in metal-working fluids; however, the relationship they have to health and disease problems is not well understood [7].

6 TESTING FOR CONTAMINATION

Test methods are vital in the fight to control and prevent microbiological contamination in fluid concentrates and coolant systems through the expeditious and accurate diagnosis and treatment of the problem. Many test methods exist, and each has its own set of advantages and limitations. The best method will vary by situation, but ideally it should balance ease of use with accurate, practical, and timely results. It is important to remember that different testing methods measure different aspects of microbial contamination.

Changes in fluid or system properties such as odor or slime formation, corrosion, emulsion splitting, and color changes are a good indication of microbiological problems. However, by the time these symptoms arise, microorganism populations may be very high and fluid properties greatly impaired. Other methods estimate the amount of microbial growth present through either direct or indirect measure of the biomass growing in the fluid.

The most common direct procedure includes taking microscopic counts. Requiring observation by a trained professional, this method is tedious and time-consuming but yields results within a matter of minutes. Another direct method that requires a skilled professional is staining. This identifies both live and dead cells and specific groups of organisms. Direct methods can also help account for organisms that will not grow on the various nutrient media specifically designed for enumerating microorganisms. However, because of their sophistication, direct test methods are not typically implemented in plants using metal-working fluids.

Indirect measures include obtaining estimates of the number of organisms present through the replication of these organisms, and obtaining measurements of microbiological activity that translate into the amount of microbial biomass present in the system. Standard plate counts and dipslide counts are the most common indirect methods for enumerating numbers of bacterial or fungi. Here, counts are estimated based on the development of bacterial or fungal colonies on the surface of solid nutrient media. In a standard plate count, a serial dilution is made of the metal-working fluid onto sterile petri dishes. The dishes are then filled with nutrient agar. Agar is liquid above 45°C but solidifies at room temperature. After several days of incubation, bacteria and fungi form visible colonies on the agar and can be visually counted. Dilutions are taken into account in determining the number of organisms in the original sample.

Because plate-count methodology can be expensive and time-consuming, a similar method has been developed that uses paddles coated with the agar media to form a dipslide. The dipslide is immersed into a fluid sample for a few seconds, returned to its sterile holder, and incubated for several days. Dipslides generally contain an indicator that turns red as bacteria or fungi begin to grow, which provides a simple visual way to determine colony counts. An additional benefit of many dipslide paddles is their ability to test for bacteria and fungi at the same time by offering different growth mediums on each side of the paddle.

In both standard plate-count and dipslide methodology, the assumption is made that each colony comes from a single cell; however, cells often aggregate together, invalidating this conclusion. In addition, a given nutrient medium will only support the growth of certain microbes and may actually inhibit the growth of others, thereby limiting the ability to gain an accurate count of the total organisms present. It is estimated that direct count methods recover only about 10% of the organisms present. Another major drawback to plate-count methods is the time required for the organisms to grow. Typically, results are available in 24 to 72 hr, but they may take longer. This provides ample time for microorganism levels to reach detrimental levels in plant environments. The long lag times associated with both plate and dipslide methods have prompted a search for more rapid techniques. Rapid test methods focus on the determination of the concentration of cell constituents such as proteins, enzymes, lipids, or ATP (adenosine triphosphate, the energy unit of living cells). While these methods provide reliable esti-

mates of microbial growth, they often require costly and complex instruments. However, as they become more commonplace, the cost of these technologies is likely to decline.

7 TREATMENT OPTIONS

Because metal-working fluids provide an environment conducive to microorganism growth, prevention techniques are vital to minimize the threat of contamination and to facilitate smooth, consistent operations. Both chemical and physical methods can be used, and often a combination of various methods is warranted when trying to establish microbiological control.

7.1 Chemical

Biocides are the most common method for controlling microbiological growth in metal-working fluids. Used to reduce or maintain bacteria and fungi at acceptable levels in water-based concentrates and final use-diluted fluids, the use of biocides ultimately maintains the integrity of the final product. While they are capable of eradicating microbial growth at high rates, due to economic constraints, biocides are more often used at rates that control growth and manage contamination.

Governmental agencies in most countries regulate the use of biocides. In the United States, they are regulated by the Environmental Protection Agency (EPA), under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) of 1972, and must meet certain toxicological and environmental impact standards. Biocides are approved based on the relative risk resulting from their use. The EPA requires that all biocide labels include specific end-use applications, and it is up to the user to determine if a registered biocide is appropriate for a specific application. Metal-working fluids are a specific EPA end-use application, and of the many chemicals registered as biocides for this end use, fewer than a dozen are routinely used by fluid formulators and end users.

Two main biocide categories exist: bactericides and fungicides. Though some biocide chemistries possess both capabilities, it is common to use both a bactericide and a fungicide to preserve a fluid.

A brief summary of the most common chemistries follows. For a more complete listing of biocides and their properties, several excellent references on the subject exist including, Paulus [8] and Ash and Ash [9]. Biocide suppliers are another valuable source of information and have product information and material safety data sheets (MSDS) that provide detailed information on biocide chemistry, efficacy, toxicological properties, and handling. Additionally, appropriate biocide labels should be consulted before determining dosages for a particular metal-working fluid application, as following dosage rates given here are only estimates. Dosage rates also vary tremendously depending on fluid formulation, housekeeping practices, time of year, operating temperature, pH, and type of contamination likely to be encountered. Testing should also be performed to determine the optimal biocide dosage.

7.2 Popular Chemistries

Formaldehyde condensates are by far the most popular and proven biocide chemistries for metal-working fluid applications. They control microbiological growth through their ability to generate formaldehyde. Like other aldehydes, the antimicrobial activity of formaldehyde is derived from an electrophilic active group that reacts with nucleophilic cell sites. These targets include functions such as amino and thiol groups as well as the amide groups of amino acids or proteins, which are often important components of enzymes or other functional proteins critical to cellular function. Because of this more generalized mode of action, formaldehyde-condensate biocides exhibit a broad spectrum of antimicrobial activity but are viewed as more effective against bacteria than fungi. One disadvantage of formaldehyde is the tendency of microorganisms to develop a resistance to it [10,11]. Because formaldehyde has a rather nonspecific mode of action, resistance development is less frequent than with other antimicrobial agents.

Triazine (hexahydro-1,3,5-tris-[hydroxyethyl]-s-triazine; CAS# 4719-04-4) is the most commonly used and most cost-effective formaldehyde-condensate biocide for metal-working fluids. It is manufactured and sold under various tradenames by specialty chemical companies including Arch Chemical, Buckman Laboratories, and Troy Corporation. An alternative form of triazine, hexahydro-1,3,5-triethyl-s-triazine (CAS# 7779-27-3) is also registered for metal-working fluid applications through R. T. Vanderbilt. Like most formaldehyde-condensate biocides, triazine is compatible with a variety of metal-working fluid components. Although triazine is viewed primarily as a bactericide, it can exhibit fungal efficacy at higher dosage rates. Dosage rates vary from about 500 to 2000 ppm active triazine, and it can be added to both metal-working fluid concentrates or directly to use-diluted fluid.

Oxazolidines are another commonly used formaldehyde-condensate biocide chemistry and include such compounds as 4,4-dimethyl-1,3-oxazolidine (CAS# 51200-87-4) and 7-ethyl bicyclooxazolidine (CAS# 7747-35-5), among others. Oxazolidines are sold under various tradenames by specialty chemical companies including The Dow Chemical company, Arch Chemical, Troy Corporation, and Creanova. In addition to the antimicrobial properties of these products, their amine nature and high base strength make them particularly stable in the high-pH environment found in most metal-working fluids. Like triazine, oxazolidines are mainly bactericidal in activity but can demonstrate fungal activity at higher concentrations. Dosage rates are generally 750–1500 ppm active ingredient. Although oxazolidines are most often incorporated as preservatives in metal-working fluid concentrates, they can also be used as tankside additions.

Tris-(hydroxymethyl) nitromethane (CAS# 126-11-4) is a formaldehyde-releasing biocide approved for use in metal-working fluid applications and available through The Dow Chemical Company. Considered a bactericide, it has a rapid speed of kill compared to most of its counterparts. Tris-(hydroxymethyl) nitromethane decomposes to release formaldehyde and thereby exerts its antimicrobial activity. It is very stable at acidic pH levels (<6), and fluid pH must be above 7.5 for this molecule to decompose and release formaldehyde. Because the tris-(hydroxymethyl) nitromethane molecule decomposes rapidly at high pH levels and lacks the stability and persistence required by fluid concentrates, it is recommended for tankside addition only. Its quick-kill properties make tris-(hydroxymethyl) nitromethane an ideal

choice in applications requiring rapid bacterial reduction. Additionally, this chemistry is particularly effective in helping to prevent "Monday morning odor" through dosing systems prior to shut down. It is often used in aluminum rolling applications where quick-kill, less alkaline, and halogen-free chemistries are preferred. Tris-(hydroxymethyl) nitromethane also works very well in combination with isothiazolinone biocides, especially in aluminum rolling applications [12]. Dosage rates are 1000–2000 ppm active ingredient to achieve bacterial control in use-diluted fluids.

A blend of 4-(2-nitrobutyl) morpholine (CAS# 2224-44-4) and 4,4'-(2-ethyl-2-nitrotrimethylene) dimorpholine (CAS# 1854-23-5) is available through The Dow Chemical Company and has proven efficacy as an antibacterial and antifungal metal-working fluid biocide. Although the active ingredients are formaldehyde-based, this blend does not exert its antimicrobial effect through the release of formaldehyde. With limited water solubility and high oil solubility, these active ingredients formulate well into many metal-working fluid concentrates, especially water-soluble oils. In fact, it is one of the few oil-soluble fungicides available. To optimize both its fungal and bacterial efficacy, it should be dosed at 500–1000 ppm active ingredient.

Phenolic compounds, including the most commonly used active ingredient 2-phenyl-phenol (OPP; CAS# 90-43-7) as well as the sodium salt of OPP (CAS# 6152-33-6), have long been used as biocides in metal-working fluids. While environmental concerns have at times lessened their popularity, these compounds have seen a resurgence due to their proven favorable human toxicity profile and restrictions prohibiting the release of metal-working fluids into the environment. As a biocide, OPP can be used either tankside or in metal-working fluid concentrates. The sodium salt of OPP has greater solubility in aqueous systems. OPP is more easily formulated into concentrates with low water contents. The compound is very broad-spectrum, having efficacy against bacteria and fungi including both yeast and molds. Both OPP and sodium OPP can be used over a broad pH range; however, performance and solubility are best at a pH above 9. Dosage rates range from about 500–1500 ppm active ingredient for OPP, and 500–1000 ppm active ingredient for the sodium salt of OPP. These active ingredients are available for various formulations from The Dow Chemical Company and Bayer in both solid and liquid forms. Another phenolic compound available from Bayer is parachlorometacresol or 4-chloro-3-methyl-phenol (CAS# 59-50-7). A very broad-spectrum biocide, parachlorometacresol is effective against bacteria, yeasts, and mold at dosages of 500–2000 ppm active ingredient. The active ingredient 4-chloro-3-methyl-phenol is effective in a pH range of 4–8 but is less stable at an alkaline pH than either OPP or sodium OPP. It can be added to metal-working fluid concentrates or used as a tankside additive. As a tankside addition, it is generally preferable to make a solution rather than adding the dry powder directly.

The biocide 2,2-dibromo-3-nitrilopropionamide (DBNPA; CAS# 10222-01-02) has recently seen increased use in metal-working applications. This biocide chemistry is viewed as a bactericide with quick-killing properties that are achieved at very low dosage rates. Manufactured by The Dow Chemical Company and Dead Sea Bromine. DBNPA is meant for use only as a tankside treatment. Because of the short half-life of DBNPA at a pH of greater than 8, this chemistry is not persistent enough to provide prolonged preservation when added to metal-working fluid concentrates. An effective dosage rate for DBNPA in tankside applications is 1–2 ppm active ingredient. More recently, a timed-release tablet [13] has been developed that provides a

slow, continuous dose of DBNPA of 0.5–1 ppm active ingredient to central systems. The tablet eliminates the need for pumping liquid material tankside and is especially useful in smaller sumps.

Several isothiazolinone chemistries have also seen extensive use in metal-working fluid applications. A combination of the active ingredients 5-chloro-2-methyl-4-isothiazoline-3-one (CMIT; CAS# 26172-55-4) and 2-methyl-4-isothiazolin-3-one (MIT; CAS# 2682-20-4) in a ratio of 2.7:1 (CMIT:MIT) is the most commonly used isothiazolinone chemistry and is supplied primarily through Rohm and Haas. This combination is effective against bacteria and fungi, including both yeasts and molds, and can be used in all fluid types. Like formaldehyde condensates, isothiazolinones are strong electrophilic agents that react with nucleophilic cell entities to exert their antimicrobial effect. Although resistance of microbial populations to isothiazolinones has been reported [14], its development was strongly affected by the dosing pattern of the biocide. When a regimen of fewer high-dose biocide treatments is compared to more frequent low-dose treatments, with the total biocide addition being equal, the low-dose treatment regimen is more likely to result in selection of resistant microbial populations. Stable over a pH range of 3–9.2, this combination chemistry shows greater stability at the lower end of the pH range. While isothiazolinone chemistry is compatible with a wide variety of metal-working fluid additives, it is incompatible with reducing agents, various amines, mercaptobenzothiazole corrosion inhibitors, and the biocide sodium 2-pyridinethiol-1-oxide.

Due to the incompatibility of isothiazolinones with certain amines (especially at higher concentrations) and the issues of sensitization that could result from using high levels of isothiazolinones in concentrates, the CMIT/MIT blend is used in tankside applications only and is not added to metal-working fluid concentrates. Combining CMIT/MIT with formaldehyde condensates or copper [15] has been shown to stabilize the isothiazolinone molecules, suggesting that these combinations may be better suited for fluid concentrate use.

Another isothiazolinone chemistry, 2-*n*-octyl-4-isothiazolin-3-one (CAS# 26530-20-1) is also appropriate for use in metal-working fluids. Unlike CMIT/MIT, MIT, which demonstrates broad-spectrum activity, 2-*n*-octyl-4-isothiazolin-3-one functions only as a fungicide. Stable in the pH range of 2–10 and compatible with a wide variety of metal-working fluid additives, 2-*n*-octyl-4-isothiazolin-3-one products are often used in combination with other metal-working biocides including CMIT/MIT, triazine, oxazolidines, and sodium pyrithione. Use with sulfides, mercaptans, bisulfites, and metabisulfites, and strong oxidizing agents, however, should be avoided. It may be added to concentrates or use-diluted fluids as a tankside addition. Dosage rates range from 25–75 ppm active 2-*n*-octyl-4-isothiazolin-3-one based on the final use-diluted fluid. This biocide is available from Rohm and Haas.

Another biocide chemistry used as a fungicide in metal-working fluid applications is 3-iodo-2-propynyl butyl carbamate (IBPC). Available in both powder and liquid forms, it has very limited water solubility but is miscible in both alcohols and aromatics. Effective dosage rates for IBPC range from 200–2000 ppm active, and it can be formulated into metal-working fluid concentrates or used as a tankside additive. The compound is available in various formulations from specialty chemicals manufacturers Arch Chemical, Troy, and Creonova.

Sodium-2-pyridinethiol-1-oxide (sodium pyrithione), a broad-spectrum fungicide, can be added either to water-based metal-working fluid concentrates or

tankside into use-dilute fluids in metal-working fluid sumps. It has an effective pH range of 4.5–9.5 and is compatible with most metal-working fluid formulations; however, it is not recommended for use in combination with CMIT/MIT-based biocides. Strong oxidizing or reducing agents also reduce the efficacy of sodium 2-pyridinethiol-1-oxide. The appearance of a blue color or black specks is common with this chemistry as it reacts with ferric ions to form ferric pyrrhione, which, incidentally, also has antifungal properties. Dosage rates range from 46–64 ppm active sodium 2-pyridinethiol-1-oxide. It is available from Arch Chemical.

7.3 Biocide Blends

Blending biocide active ingredients is a popular practice and works to broaden or complement the antimicrobial spectrum of a singular product. Here, an antifungal product may be combined with an antibacterial product to provide a dual mode of action, or in cases where an antibacterial biocide may have limited efficacy against certain bacteria, another antibacterial agent may be added to expand the system's overall bacterial efficacy. For example, sodium 2-pyridinethiol-1-oxide, a proven fungicide, is often blended with triazine or oxazolidines, both proven bactericides, to form a blend effective against both types of organisms. An added benefit of commercial blends is that they reduce the number of products that an end-use site must inventory.

Biocides may also be blended together to improve the overall performance of either biocide. This concept, known as synergy, can boost efficacy in several different ways. One biocide molecule may stabilize another while broadening the spectrum of antimicrobial coverage or providing additional modes of action for killing or inhibiting microorganisms. The use of isothiazolinones with certain formaldehyde-condensate biocides is an example of this type of synergistic blend [16]. Isothiazolinone molecules, when used alone, have limited persistence in metal-working fluids. However, the formaldehyde condensates stabilize the isothiazolinones and increase the persistence of the blend.

It is important to remember that in the United States, regulations regarding blending of registered biocides are much stricter than current regulations are in other parts of the world. If a blend is preformulated in the United States, the blend itself must be registered by the EPA, separately, as a pesticide. Currently, the same restrictions do not apply worldwide; however, with regulatory initiatives such as the European Biocidal Products Directive, tighter biocide regulations are expected worldwide.

7.4 Methods of Biocide Application

Biocides can be either formulated into the metal-working fluid concentrates or added to a system tankside. Each strategy has advantages and limitations, and the biocide chemistry may dictate which application method is best. A biocide added into a concentrate will not only protect the concentrate but will provide antimicrobial protection in the use-diluted fluid as well. This method of biocide addition reduces handling of the concentrated biocide at plant locations and end-use sites and ensures that the biocide is added proportionally to the systems in the correct ratio to the fluid. The limitation to this type of addition is that different metal-working fluid systems may exert different demands on the biocide. For instance, there may be compounds in a central system that are not compatible with a certain biocide chemistry. Thus, the biocide in the newly diluted fluid may be deactivated and consequently fail.

In systems that are already heavily contaminated, the organisms may create a demand on the biocide and rapidly deplete it, leaving the remaining formulation components unprotected. In addition, adding a biocide to the concentrate for preservation of the use-diluted fluid assumes that the fluid will be diluted properly at the end-use site. If for any reason the fluids are overdiluted, biocide levels may not be sufficient to control microbiological growth.

Alternatively, tankside addition of a biocide at the plant site allows a more direct and specific way to address individual plant situations. With this method, biocide selection can be based on unique plant operating parameters such as water quality (microbiological and chemical), housekeeping, fluid residence time, degree of expertise in personnel, and waste treatment processes used in the plant. Tankside treatment does require close, if not constant, monitoring, but the added benefit of this is the ability to respond immediately to problems as they arise. Routine tankside addition of a biocide, with specific targeted levels of biocide in the fluid, is more likely to provide effective control if these levels are maintained at all times. It is better to integrate biocide use into a planned program than to use it on an as-needed basis. Waiting until a microbiological problem arises before providing treatment may result in large amounts of dead microbial biomass, which can plug pipes and filters and release odors associated with decaying microbial cells. Limitations associated with tankside treatment include user concerns about maintaining and handling neat (concentrated) biocide products due to the health and safety issues associated with these products, and the labor-intensive aspect of having to constantly monitor and maintain biocide levels. Tankside addition also requires more in-depth training in the proper handling of biocides, as well as a deeper understanding of how to properly calculate and add a given dose of biocide. When using tankside treatment methods, it is very important that all personnel in the plant be informed of the necessary precautions to take when neat biocides are present.

Many metal-working fluid operations use both methods of biocide application to provide a comprehensive treatment program. While biocides added to fluid concentrates help preserve the concentrate and help reduce the volume of tankside preservative that must be kept on-site, they also may become depleted over time. The routine addition of a tankside biocide, once the biocide provided in the concentrate has been depleted, prevents uncontrolled microbial growth and ultimately helps extended fluid life.

7.5 Biocide Selection

Though a seemingly straightforward task, biocide selection can prove challenging because of the number of options available and the fact that no single biocide will provide optimum performance in all situations. Of the various factors to consider when choosing a biocide, the first should be whether the product has an EPA end-use registration for metal-working fluid applications. In addition, the compatibility of the biocide with the fluid must be considered. The biocide must not affect the functional properties of the fluid, including lubricity, corrosion inhibition, or emulsion stability. Other factors such as cost, known chemical incompatibilities, and mode of application also need to be examined before laboratory or field evaluation of the biocide can begin. The type of metal on which the fluid is being used should also be considered, as ferrous and nonferrous metals may have different compatibility with various biocides.

Biocides must also be cost-effective and protect against the spectrum of microorganisms affecting the fluid. While a variety of laboratory test methods is available for measuring biocide performance, simulating real-use conditions in metal-working systems is difficult. The most commonly used standard procedures for testing biocides in metal-working fluids are those sanctioned by the American Society for Testing of Materials (ASTM). Testing methods include ASTM D3946-92 [17] and E686-91 [18]. These relatively straightforward and simple ASTM protocols do a reasonable job of predicting biocide efficacy. Test method ASTM D3946 was originally developed as a measure of bioresistance of metal-working fluids, but has also been adapted for use as a short-term biocide efficacy testing method. In this method, one-liter samples of use-diluted metal-working fluids are initially inoculated with bacteria and fungi and microbial counts are taken over time under various conditions of aeration. This method is generally used as a quick biocide screening method because its ability to predict longer-term preservation of metal-working fluids is limited.

ASTM E686-91 is another method often used for biocide selection and was specifically designed for evaluating antimicrobial agents in metal-working fluids. Here, as in ASTM D3946, one-liter samples of use-diluted metal-working fluids are initially inoculated with bacteria and fungi and microbial counts are made. Then a five-day work schedule is simulated for a six-week period with the samples aerated for five days, then left stagnant for two, and reinoculation occurring weekly. Because this method provides a much more severe microbiological challenge than does ASTM D3946, many formulators and users run ASTM D3946 on a large number of biocide candidates to narrow the field, and then subject the top performers to ASTM E686-91 for further evaluation. Despite the best efforts and assumptions, laboratory testing is not a perfect indicator of real-use conditions. Consequently, when a biocide has been chosen for a system based-upon laboratory trials, it is best to confirm the laboratory results with a field trial.

7.6 Biocide Handling

It is important to remember that biocide molecules are designed to control and arrest microbiological growth and, therefore, they have toxic properties. Special precautions should always be taken when handling biocides. A product's material safety data sheet (MSDS) is the best resource to consult, as it will present comprehensive information on the proper handling methods for that particular biocide chemistry. Although the recommended types of protection will vary by biocide, in the interest of good chemical hygiene, gloves, aprons, and eye and face protection are recommended when handling any biocide.

7.7 Physical and Nonchemical Control Methods

Although chemical methods are the most common means of controlling microbiological growth in metal-working fluids, several nonchemical methods have received attention. These include heat treatment or pasteurization, UV treatment or irradiation, and filtration. Compared to chemical treatments, these technologies share some common disadvantages. Because these methods treat metal-working fluids at a single point in a system, microbiological growth that may not be circulating in the fluid, or is help up in dead areas of the system or in biofilms, is not treated.

Pasteurization of metal-working fluids heats the fluid to a temperature high enough to destroy the microorganisms responsible for fluid deterioration, but, temperate enough to maintain the functional properties of the fluid. While many microorganisms are particularly susceptible to heat treatment, others are more thermotolerant and survive this treatment, leaving surviving microorganisms to degrade the fluid. This process is also energy-intensive, requiring fluids to remain at about 142°C for periods of greater than 30 minutes. Consequently, the success of this method depends on the availability of an affordable energy source and the feasibility of heating the fluid of an entire system. While Elsmore and Hill [19] obtained good results with heat treatment, they found that heat-resistant populations developed upon intermittent pasteurization.

Several types of radiation technology can prove useful in controlling microbial growth in metal-working fluid systems, including ultraviolet (UV) irradiation, high-energy electron irradiation, and gamma irradiation. With all these methods, fluids flow through an irradiation bank contained in a thin-film layer. The radiation causes lethal mutations or kills organisms by direct ionizing effects. All three methods have at least some degree of difficulty penetrating opaque materials like metal-working fluids. UV technology is probably the least effective due to this challenge, followed by high-energy electron radiation, which is also energy-intensive, making it less cost-effective. Gamma irradiation offers the most potential in penetrating fluids and killing organisms; however, handling of this radiation source is costly and requires well-trained personnel [20].

Filtration systems are designed to remove particulate material from fluid streams; however, they do not necessarily remove microbial cells directly. Microbial populations tend to grow on particulate surfaces rather than in free-flowing fluids. By removing these particles, filtration systems can keep metal-working fluids cleaner and, therefore, less vulnerable to microbial growth. Naturally, cleaner systems often require less biocide. It is important to remember, however, that filters can also harbor microorganisms and may actually add to contamination problems.

Currently nonchemical treatment methods remain largely unpopular for metal-working fluid applications because of their significant capital expenditures and energy costs. However, as pressure to remove toxic chemicals from fluid formulations increases, there may be a greater impetus for the industry to adopt more of these nonchemical treatment technologies.

7.8 Bioresistant Fluids

Today's metal-working operations, emphasize extending fluid life as long as possible. Not only does this reduce waste disposal costs, but customers would also like to eliminate or reduce the concentration of fluid components viewed as toxic, such as biocides. In an attempt to reach these goals, considerable effort has been spent on trying to formulate fluids from bioresistant materials. A bioresistant material is one that, while not killing microorganisms, is not readily decomposed by microbial attack. Bioresistant materials do not provide a readily available food source for microorganisms, but at the same time these materials cannot stand up to repeated insults of microbial contamination. Bioresistant fluids are also not subject to the requirements for U.S. EPA registration under FIFRA.

A metal-working fluid's overall potential for microbial degradation depends on the susceptibility of each of its raw materials to microbial attack. A bioresistant component remains unchanged in structure and functional properties in the presence of a microbial population. Bioresistant fluids do not necessarily have lower counts of microorganisms, and inhibition of microbial activity or growth is not necessarily a property of a bioresistant raw material. One metal-working fluid component that has received considerable attention in regard to this characteristic is alkanolamines. While all alkanolamines eventually become susceptible to biodegradation, their specific bioresistance characteristics can vary [21,22]. In general, 2-amino-2-methyl-1-propanol (AMP) appears more bioresistant than diglycolamine (DGA), monoethanolamine (MEA), and triethanolamine (TEA); however, differences exist in bioresistance of these alkanolamines depending on the fluid formulation and the situation in which the fluid is being used. At least a portion of the bioresistance attributed to alkanolamines appears to be related to pH. Rossmore [22] showed that high pH attributed to alkanolamines provides a degree of bioresistance. However, in some fluids, bioresistance was maintained when pH was lowered, while in others bioresistance was lost. Sandin et al. [23] report that bioresistance of metal-working fluids was directly proportional to pH and alkyl chain length of the particular ethanolamines tested.

Amine salts of boric acid function as ferrous metal corrosion inhibitors. A major side benefit of these salts is that they resist microbial attack [24]. However, they tend to form hard and/or sticky residues on machines and parts [25].

8 THE FUTURE OF MICROBIOLOGICAL CONTROL

Although the metal-working fluid industry is not viewed as an aggressively expanding market, it is full of impending changes and challenges. Metal-working operations and fluid technologies will continue to become more sophisticated. As many experts predict, this will drive the use of synthetic and semisynthetic fluids and end-use dilutions, increasing the demand for innovative and effective microbial control strategies. Environmental restrictions regarding fluid disposal are also likely to escalate, increasing disposal costs and creating even more pressure to extend fluid life. Today's popular option of simply adding more biocide to increase fluid utility will likely see counter pressure as safety-conscious workers demand the use of less toxic fluids. As environmental and exposure concerns increase, the industry's biocide options will decrease as more biocidal substances come under regulatory pressure. In addition, microbial resistance will continue to reduce the efficacy of current biocides. New chemistries coming to market are also anticipated to slow due to the high cost of registering new active ingredients. These are the industry's challenges, but they will also serve as the impetus for the advancement of the industry and evolution of the next generation of microbe control strategies in which bioresistant fluids, nonchemical treatments, and lower-toxicity biocide technologies will all play a key role.

REFERENCES

1. K.L Buers, EL Prince, CJ Knowles. The ability of selected bacterial isolates to utilize components of synthetic metalworking fluids as sole sources of carbon and nitrogen for growth. *Biotechnol Lett* 19:791-794, 1997.

2. M Abanto, J Beyers, H Noble. The effect of tramp oil on biocide performance in standard metalworking fluids. *Lub Eng* 50:732–737, 1994.
3. RG Almen et al. Application of high-performance liquid chromatography to the study of the effect of microorganisms in emulsifiable oils. *Lub Eng* 38:99–103, 1982.
4. HW Rossmore, LA Rossmore. Effect of microbial growth products on biocide activity in metalworking fluids. *Intl Biodetrn* 27:145–156, 1991.
5. HW Rossmore. Biostatic fluids, friendly bacteria, and other myths in metalworking microbiology. *Lub Eng* 49:253–260, 1993.
6. LA Herwaldt et al. A new *Legionella* species, *Legionella feeleeii* species, nova, causes Pontiac fever in an automobile plant. *Ann Intern Med* 100:333–338, 1984.
7. SM Kennedy et al. Acute pulmonary responses among automobile workers exposed to aerosols of machining fluids. *Amer J Ind Med* 15:627–641, 1989.
8. W Paulus. *Microbiocides for the Protection of Materials*. London: Chapman & Hall, 1999.
9. M Ash, I Ash. *The Index of Antimicrobials*. Hampshire, England: Gower, 1996.
10. M Sondossi, HW Rossmore, JW Wireman. Observations of resistance and cross-resistance to formaldehyde and a formaldehyde condensate biocide in *Pseudomonas aeruginosa*. *Int Biodeterioration* 21:105–106, 1985.
11. M Sondossi, HW Rossmore, R Williams. Relative formaldehyde resistance among bacterial survivors of biocide-treated metalworking fluids. *Int Biodeterioration* 25:423–437, 1989.
12. DF Heenan et al. Isothiazolinone microbiocide-mediated steel corrosion and its control in aluminum hot rolling emulsions. *Lub Eng* 47:545–548, 1991.
13. FJ Passman, J Summerfield, J Sweeney. Field evaluation of a newly registered metalworking fluid biocide. *Lub Eng* 56:26–32, 2000.
14. M Sondossi, HW Rossmore, ES Lashen. Influence of biocide treatment regiment on resistance development to methylchloro-/methylisothiazolinone in *Pseudomonas aeruginosa*. *Int Biodeterior Biodegrad* 43:85–92, 1999.
15. AB Law, ES Lashen. Microbiocidal efficacy of a methylchloro-/methylisothiazolinone/copper preservative in metalworking fluids. *Lub Eng* 47:25–30, 1991.
16. M. Sondossi et al. Factors involved in bacterial activities of formaldehyde and formaldehyde condensate/isothiazolinone mixtures. *Int Biodeterior* 32:243–261, 1993.
17. American Society for Testing and Materials (ASTM) Designation Test Method D3946-92, vol 5.02. Philadelphia: ASTM, 2000.
18. American Society for Testing and Materials (ASTM) Designation Test Method E686-91 (1998), vol 11.05. Philadelphia: ASTM, 2000.
19. R Elsmore, EC Hill. The ecology of pasteurized metalworking fluids. *Int Biodeterior* 22:101–120, 1986.
20. TF Heinrichs, HW Rossmore. Effect of heat, chemicals and radiation on cutting fluids. *Devel Ind Microbiol* 12:341–345, 1971.
21. U Auman, P Brutto, A Eachus. Boost your resistance: Metalworking fluid life can depend on alkanolamine choices. *Lubes'N' Greases* 6:22–26, 2000.
22. HW Rossmore. Biostatic fluids, friendly bacteria, and other myths in metalworking microbiology. *Lub Eng* 49:253–260, 1993.
23. M Sandin, I Mattsby-Baltzer, L Edebo. Control of microbial growth in water-based metalworking fluids. *Int Biodeterior* 27:61–74, 1991.
24. J Childers, L Hegman. The biostability of metalworking fluid additives for waste minimization. Presentation at the Annual Meeting of the Society of Tribologists and Lubrication Engineers, 1991.
25. J Byers. *Metalworking Fluids*. New York: Marcel Dekker, 1994.

PART II

APPLICATIONS

Additives for Crankcase Lubricant Applications

EWA A. BARDASZ

The Lubrizol Corporation, Wickliffe, Ohio, U.S.A

GORDON D. LAMB

BP Castrol, Pangbourne, England

1 INTRODUCTION

Engine oil lubricants make up nearly one half of the lubricant market and therefore attract a lot of interest. The principal function of the engine oil lubricant is to extend the life of moving parts operating under many different conditions of speed, temperature, and pressure. At low temperatures the lubricant is expected to flow sufficiently in order that moving parts are not starved of oil. At higher temperatures they are expected to keep the moving parts apart to minimize wear. The lubricant does this by reducing friction and removing heat from moving parts. Contaminants pose an additional problem, as they accumulate in the engine during operation. The contaminants may be wear debris, sludges, soot particles, acids, or peroxides. An important function of the lubricant is to prevent these contaminants from doing any damage.

To function effectively, the lubricant needs chemical additives as well as base oils. Depending on the application, various combinations of additives are used to meet the required performance level; the most important are listed below:

- Detergents
- Dispersants
- Antiwear
- Antioxidants
- Viscosity modifiers
- Pour point depressants
- Foam inhibitors

In addition to these, there are several more additives for anticorrosion, antirust, seal swelling, biocide, and demulsability.

2 DETERGENTS

2.1 Introduction

Detergents play an essential role in protecting various metallic components of internal combustion engines by neutralizing acidic compounds formed during combustion processes [1–3]. Gasoline and diesel engine oils account for over 75% of total detergent consumption. Detergent treatment in engine lubricant can reach 6–10 wt%, with marine diesel engine lubricants containing the highest concentration levels due to combustion of high-sulfur fuel, which leads to formation of inorganic acidic combustion products such as sulfuric acid.

The purpose of detergents in crankcase oils is

1. To suspend/disperse oil-insoluble combustion products, such as sludge or soot and oxidation products
2. To neutralize combustion products (inorganic acids)
3. To neutralize organic acids products of oil degradation processes
4. To control rust, corrosion, and deposit-forming resinous species [4]

Why are these specific functions critical to engine durability? Coke and varnishlike deposits can restrict the free movement of the piston rings, allowing a portion of the combustion gases to pass into the crankcase or combustion chamber, leading to heavy contamination of the oil, impacting engine out emissions, and even causing piston seizure if the engine operates at high loads [5]. Heavy sludge can plug oil filters, leading to oil starvation and thus to catastrophic wear especially during cold-temperature start-ups [6]. Acidic fuel combustion products can cause corrosion.

Detergents can react with the hydroxyacids, deposit precursors, formed during the oxidation of the oil. Deposit precursors are attracted to detergent micelles and trapped within them and, thus, cannot settle out onto metal surfaces and form resinous deposits. The cleaning action of detergent additives is attributed to chemisorption processes and formation of metal salts.

In order to satisfy the above-mentioned requirements, practically all detergent additives contain

Polar head: hydrophilic, acidic groups (e.g., sulfonate, hydroxyl, mercapton, carboxylic, or carbonamide groups) that react with metal oxides or hydroxides

Hydrocarbon tail: oleophilic aliphatic, cycloaliphatic, or alkyaromatic hydrocarbon radicals that provide oil solubility

One or several metal ions

Idealized representation of the detergent structures is shown in [Figure 1](#).

Although several metals have been incorporated into detergents, only three metal cations are now commonly used—calcium, magnesium, and sodium. Heavy metals such as barium are no longer used.

Detergents are described chemically in terms of their metal ratio, soap content, percent sulfate ash, degree of overbasing or conversion, and total base number (TBN) [2]. The metal ratio is defined as total equivalents of metal per equivalent

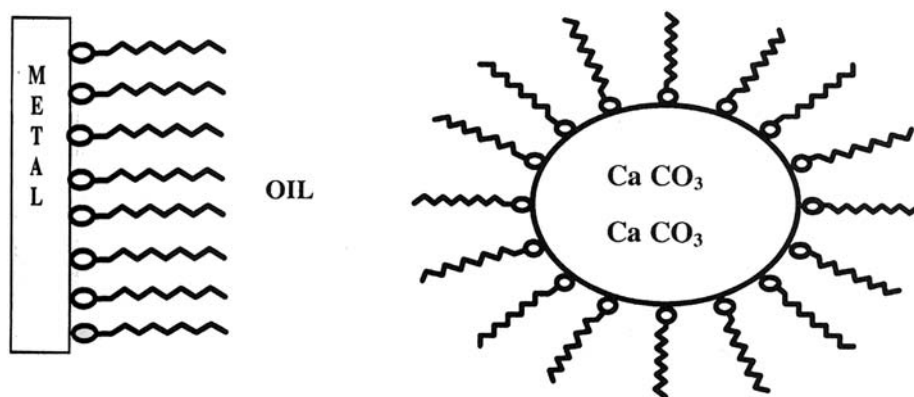


Figure 1 Idealized representations of neutral and overbased detergents.

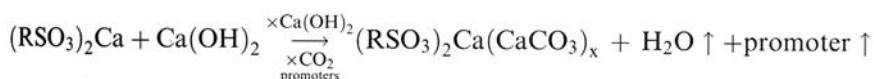
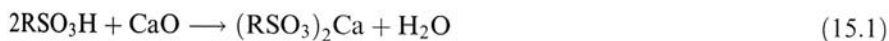
of sulfonate acid. Soap content refers to the amount of neutral salt and reflects the detergent's cleansing ability, or detergency. The percent sulfate ash is the ash obtained after treating the detergent with sulfuric acid and complete combustion. The degree of overbasing (conversion) describes the ratio of equivalents of the metal base to equivalents of the acid substrate and is usually expressed as conversion. Conversion provides the amount of inorganic material relative to that of the organic material and is expressed as number of equivalents of base per equivalent of acid times 100. The overbased part of detergent is needed to neutralize acid byproducts. The total base number (TBN) indicates its acid-neutralizing ability and is expressed as mg KOH/g of additive. It is measured using a potentiometric method (e.g., ASTM D2897).

The alkaline reserve of all modern detergents may vary considerably. Neutral detergents contain the stoichiometric amounts of metals, corresponding to the basicity of the acids. Basic (or overbased) detergents contain a significant excess of metal oxides, hydroxides, carbonates, etc. in colloidally dispersed form. The structure of detergents can be envisioned as a reverse micelle, with an amorphous carbonate molecule encapsulated by metal soap molecules with their nonpolar ends extended into the oil (Figure 1).

In practice, virtually all commercial detergents are overbased to some extent. For example, commercial "neutral" sulfonates have a TBN of 30 or less. "Basic" detergents have a TBN of 200 to 500.

Some detergents can act as oxidation inhibitors, depending on the nature of their functional group. Most modern motor oils contain combinations of the several detergent types, which are selected to give optimum performance.

Preparation of calcium detergents can be represented schematically as follows:



2.2 Sulfonates

The salts of long-chain alkylarylsulfonic acids are widely used as detergents. Basic calcium sulfonates make up 65% of the total detergent market.

As the demand for sulfonic acids has rapidly increased, synthetic products with the general structure $(\text{RSO}_3)_y\text{Me}_w(\text{CO}_3)_x(\text{OH})_y$ are also used besides the sulfonated alkylaromatics from petroleum refining known as “natural” sulfonates. Synthetic products are produced by the sulfonation of suitable alkylaromatics, e.g., the dialkylation and polyalkylation products from the dodecylbenzene production; their alkyl radicals should contain together at least 20 C atoms. Other starting materials are alpha-olefin polymers with mean molecular masses around 1000.

The neutral sulfonates (schematically shown in Figure 2) contain the stoichiometric amounts of metal ion and acid. In addition to Na, Ca, and Mg, patents have been issued describing detergents containing tin, chromium, zinc, nickel, and aluminium; however, the importance of these metals is inferior to that of the alkaline-earth metals.

Neutral oil-soluble metal petroleum sulfonates can be converted to basic sulfonates by mixing and heating with metal oxides or hydroxides, followed by filtration. In these products, the metal oxides and hydroxides are present in colloiddally dispersed form (Figure 2). Such basic sulfonates have a considerably increased alkaline reserve and thus a higher neutralizing power.

Treatment with carbon dioxide converts basic sulfonates into metal sulfonate-carbonate complexes that have the same alkaline reserve, yet a lower basicity. Efforts to produce additives with even higher neutralizing power have led to the development of the overbased sulfonates. Besides high neutralizing power, the additives also possess a high dispersing capacity, due to the large amount of polar inorganic bases present.

Overbased sulfonates are produced, for instance, by heating an oil-soluble sulfonate with metal oxides in the presence of substances that act as catalysts, such as phenols, phosphoric acid derivatives, etc.

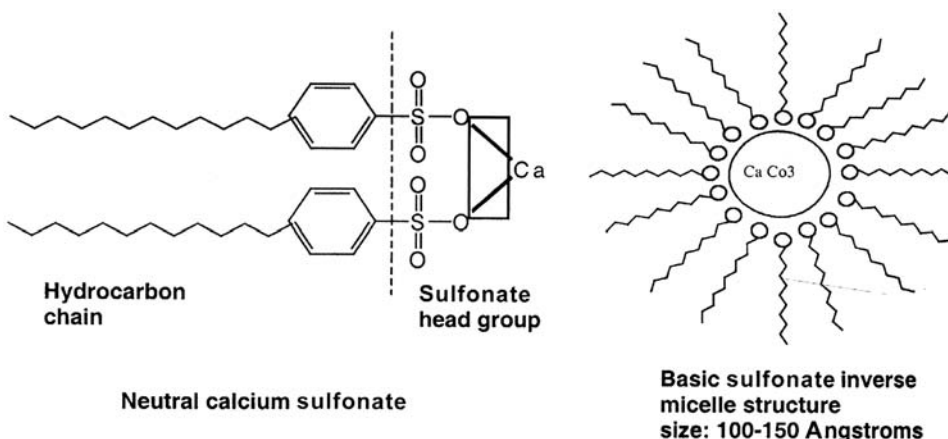


Figure 2 Natural and basic sulfonates structures.

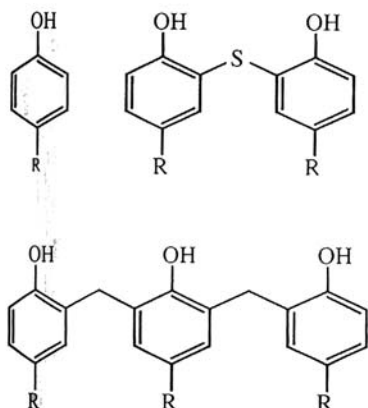


Figure 3 Phenates and sulfurized phenates structures.

2.3 Phenates, Sulfurized Phenates, and Salicylates

Basic phenates make up 31% of the total detergent market. Schematic structures of phenates and sulfurized phenates are shown in Figure 3.

Phenate detergents are available as calcium and magnesium salts. Metal salts of alkylphenols and alkylphenol sulphides, $(R)(OH)C_6H_3-S_x-C_6H_3(OH)(R)$, where $x = 1$ or 2 and R is ~ 12 C, can be prepared at elevated temperatures by the reaction of alcoholates such as Mg ethylate with alkylphenols or by the reaction of the phenols or phenol sulfides with an excess of metal oxide or hydroxide (particularly of Ca) sulfides with an excess of metal oxides or hydroxides in neutral phenates. Besides their neutralization power, phenates also possess good dispersant properties.

As in the case of the sulfonates, the phenates can be overbased. Overbased phenates are often used as components of marine diesel cylinder lubricants.

In many commercial lubricant applications, sulfonate and phenate detergents are used in combination and often various metals in order to obtain an optimum detergent action and neutralizing power. Besides better neutralizing power, the main incentive for the use of basic phenates is lower manufacturing cost compared to the normal phenates.

Salicylates are less commonly used as detergents in crankcase lubrication. The typical structure of salicylate detergent is given in Figure 4.

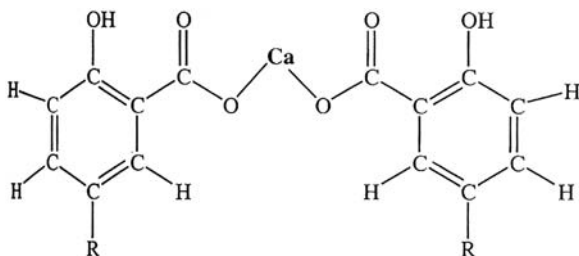


Figure 4 Calcium salicylate structure.

Besides their detergent properties, the metal alkylsalicylates also possess oxidation-inhibiting and anticorrosion properties. Their solubility in mineral oils can be improved in the case of esters by extending the chain length of the alcohol radicals or generally by alkylation of the aromatic ring. The alkaline-earth salicylates are usually overbased by the incorporation of alkaline-earth carbonates, stabilized in the form of micelles.

2.4 Other Detergents: Phosphates, Thiophosphates, Phosphonates, and Thiophosphonates

In addition to their use as oxidation inhibitors, phosphates and thiophosphates also serve in various variations and combinations as detergents. Thiophosphonates are obtained by the reaction of phosphorus pentasulfide with polyisobutenes; olefins, fatty alcohols, and esters are neutralized after hydrolysis with metal hydroxide.

2.5 Performance in Lubricants

For crankcase engine oils, which include passenger car, heavy-duty diesel, marine diesel, and stationery gas applications, detergents provide several key performance functions. One of the primary functions of overbased detergents is to neutralize acidic combustion byproducts [2–4]. In all reciprocating piston internal combustion engines, gases from the combustion chamber are forced around and through the piston rings and into the crankcase, where they interact with the lubricant. These combustion gases and byproducts contain such components as oxides of sulfur, derived from the sulfur content of fuels. Particularly in diesel engines, these sulfur oxide compounds interact with oxidized components from the fuel and base oil to produce sulfuric acid and organic acids [6].

Another form of combustion byproducts comes from oxides of nitrogen, derived from the high-temperature combination of nitrogen and oxygen from the intake air. These byproducts are predominant in gasoline engines in which the oxides of nitrogen materials can further react with water (from the combustion process), oxidized oil and fuel, and soot (if present) to produce engine sludge and piston varnish [5]. Obviously, these acidic combustion gases and byproducts are detrimental to the extended life of both engine components and the lubricant itself. They can give rise to increased rusting of steel parts and corrosion of bearings.

The use of high-TBN, overbased detergents can combat these problems. One, however, must be careful in formulating with an appropriate mix of detergents for acid control and corrosion performance. The use of several appropriate detergents in a lubricant for excellent engine rust and bearing corrosion performance may not necessarily be favorable to maintaining good valve train wear performance such as in the well-known gasoline engine specification tests, the Sequence VE and Sequence IVA (for more details regarding these tests, see Dispersants section, [Table 3](#)).

[Figure 5](#) plots data from a recent passenger car field test showing the decrease in total base number (TBN) and the increase in total acid number (TAN) with use. OEM oil drain recommendations are often determined by this type of testing. Typically, it is considered desirable to change an oil before the TBN and TAN cross. In this “severe service” example, the oil, which starts at a TBN of 6, would need to be changed twice as often as the oil that has an initial TBN of about 9. Evidence such as this results in oils with higher TBN being recommended for longer drain intervals.

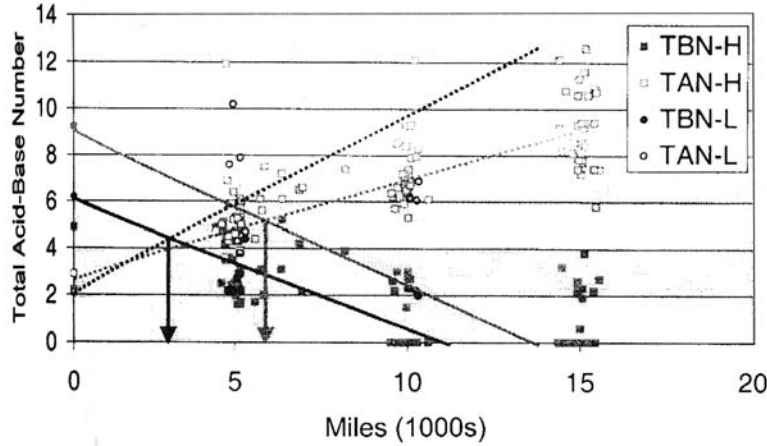


Figure 5 Passenger car field testing: TBN/TAN relation.

A second function of a detergent is to retard deposit formation on engine parts, especially parts that are operating at high temperature such as pistons and piston rings (Figure 6). Detergency of North American diesel engine oils is evaluated using both single-cylinder engine tests (Caterpillar 1N, 1K, 1P, and 1Q) and multicylinder engine tests (Cummins M11, MACK T-9 and T-10). The selection of detergents to give the best piston and ring cleanliness is highly dependent on the temperature of the piston-ring area, the metallurgy of the piston, the ring pack design, and the base stock of the lubricant being tested. Metallurgy variances in engine designs such as aluminum versus articulated steel diesel pistons complicate proper detergent selection. A particular mixture of detergents may be excellent with aluminium hardware, but may only perform marginally with steel hardware.

Some types of detergents perform additional functions in an engine oil formulation. For example, coupled-coupled alkyl phenols enhance high-temperature oxidation inhibition. Due to their specific structure and thermal stability, these detergents help prevent oxidation of the lubricant under high-speed and load engine conditions;

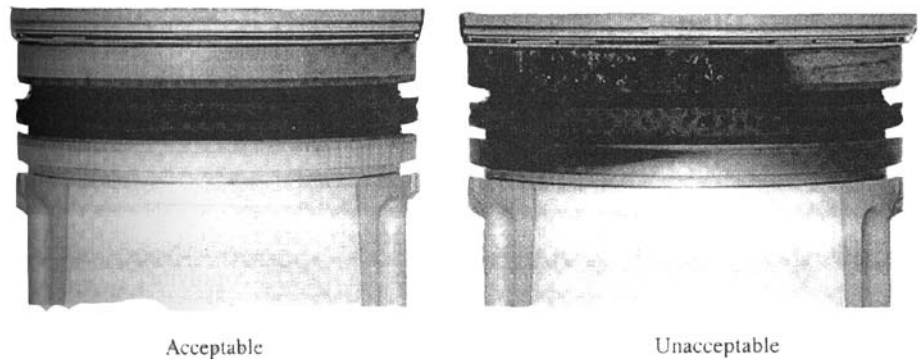


Figure 6 Detergents keep upper pistons clean.

the result is a lower viscosity increase of the oil. Of course, high-temperature oxidation inhibition synergizes with the detergent's ability to enhance "cleanliness."

In summary, the best overall cost and performance compromise with using a selected combination of detergents in a lubricant depends on many factors. Several of these factors entail complete engine performance, customer desires, and regulations including the maximum total amount of metal or metal ash allowed in a lubricant as set by specification requirements.

3 DISPERSANTS

3.1 Introduction

Dispersants are typically the highest treat additive in an engine oil formulation. They are similar to detergents in that they have a polar head group with an oil-soluble hydrocarbon tail. While detergents are used to clean engine surfaces and neutralize acidic byproducts, their effectiveness is limited when it comes to dispersing oil-insoluble products resulting from the byproducts of combustion. The principal function of a dispersant is to minimize the deleterious effects of these contaminants. The most obvious contaminants related to engine lubricants are black sludge and soot particles. Sludges range from thick, oil-like deposits to a harder deposit; soot is composed primarily of carbon particles and is typically found in diesel engines. Dispersants are used to disperse these contaminants within the engine, thereby ensuring that the oil flows freely. The dispersing ability of the dispersants helps keep the engine clean and, in some cases, will maintain piston cleanliness. Some formulators will actually refer to certain dispersants as ashless detergents.

Over many years dispersants have played a major part in keeping the engine clean, and they continue to play an important part in the oil formulation. In modern, top-quality engine oil formulations, dispersant will range from 3–6% by weight. Typically this would account for around 50% of the total oil additive in the lubricant.

3.2 Dispersant Structure

Dispersants consist of an oil-soluble portion plus a polar head group. The polar group is attached to the oil-soluble group by means of a "hook." The schematic in [Figure 7](#) gives a simplistic representation of a dispersant structure based on the reaction of a polyisobutenyl succinic anhydride (PIBSA) with either a polyamine or a polyol.

Many different types of dispersants have been used in lubricant additive packages. Over the years these have evolved as the lubricant requirements, because OEMs and the testing organizations have become more demanding. The list below, while not exhaustive, covers the most popular types of dispersant chemistries in use today:

- Polyisobutenyl succinimide

- Polyisobutenyl succinate ester

- Mannich dispersants

- Dispersant viscosity modifiers [e.g., dispersant olefin copolymer (dOCP), dispersant polymethacrylate (dPMA)]

By far the most common group of dispersants is polyisobutenyl succinimides. These are the preferred dispersants for tackling the black sludge problem that

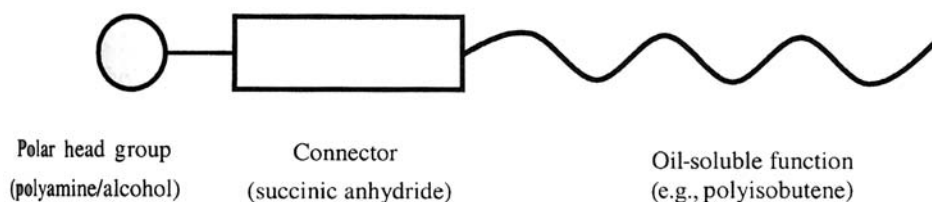


Figure 7 Schematic of a dispersant molecule.

occurred in gasoline engines during the 1980s. Since the 1990s they have also been used in ever-increasing levels to reduce oil thickening, which is a result of the high levels of soot in diesel engine oils.

To prepare a polyisobutenyl succinimide dispersant, a hook is attached by reacting maleic anhydride (MA) with polyisobutene (PIB) to make polyisobutene succinic anhydride (PIBSA). The PIBSA is then typically neutralized with a polyamine mixture to yield the succinimide dispersant (Figure 8).

The reaction between the PIB and the MA occurs via the unsaturated end group of the PIB. This can be achieved by directly reacting the PIB with MA at temperatures in excess of 200°C (direct alkylation, or DA for short). Once the PIBSA is formed, it can react again to make the disuccinated product. The reaction of the PIB and MA depends on the unsaturated end groups of the PIB being reactive enough to add to the MA. As the reaction proceeds, the addition of MA to the PIB slows as all the reactive end groups in the PIB are used up. With some types of PIBs this will leave a relatively large amount of unreacted PIB. In recent years this problem has been overcome by using PIBs with very high levels of terminal vinylidene groups, in some cases greater than 80%. These vinylidene groups are more reactive via the direct alkylation route enabling DA PIBSAs to be prepared with relatively low levels of unreacted PIB (see Figure 9).

The key to the PIB-MA reaction is to ensure that the PIB is fully converted into PIB succinic anhydride. Any unreacted PIB in the finished lubricant will result in a formulation with poor low-temperature viscometric properties. In addition, the dispersant will be less effective in preventing sludge formation and in dispersing soot since not all the oil-soluble PIB will contain active dispersant chemistry.

For these reasons it is beneficial to maximize the conversion of the PIB to the succinic anhydride. The addition of MA to the PIB is made easier by using chlorine, which catalyzes the reaction via a PIB diene intermediate, which reacts more readily

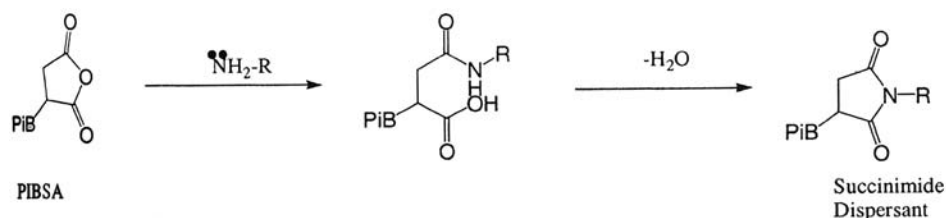


Figure 8 Imidation of a polyisobutenyl succinic anhydride.

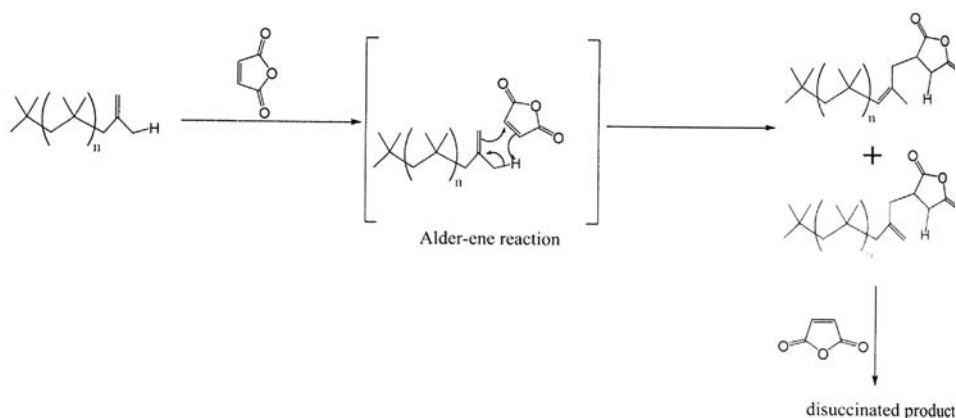


Figure 9 Direct alkylation reaction of polyisobutene with maleic anhydride.

with the MA, yielding a highly converted PIB with minimal unreacted PIB. A schematic of the reaction is shown in Figure 10.

3.3 Polyisobutene Synthesis

Polyisobutene is produced by cationic polymerization of either pure isobutene or a C_4 stream from an oil refinery. The isobutene in the C_4 refinery stream reacts preferentially, whereas other compounds such as n -butenes and butanes do not. Typical catalysts for these reactions include $AlCl_3$ and BF_3 .

The molecular weight of the PIB is very important and can have a significant effect on the dispersant performance. Typically the number average molecular weight (M_n) of PIB ranges from 500 to 3000, although there are instances where PIBs outside this range may be used. The higher-molecular-weight PIB dispersants have viscosity modifier properties and aid the formulation of multigrade oils. In addition, they are much more effective in the handling of black sludge and soot. While lower-molecular-weight dispersants have found use as sludge and soot disper-

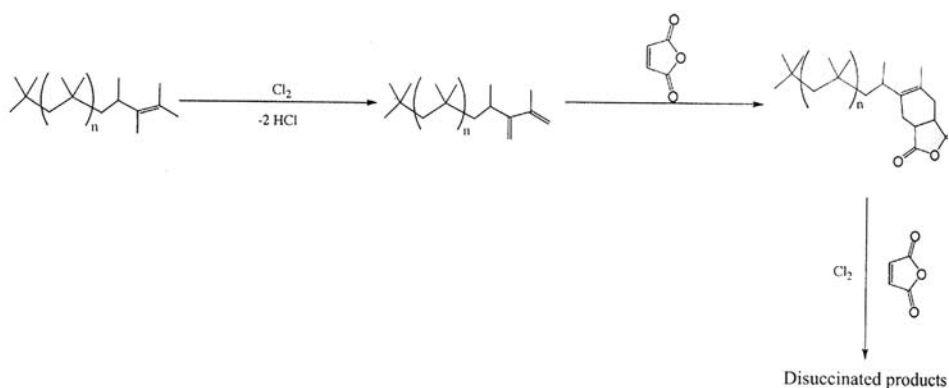


Figure 10 Chlorination/succination of PIB.

sants, they are clearly less effective. Dispersants made using higher-molecular-weight PIB ($M_n > 2500$) have an adverse effect on the low-temperature viscosity properties of the finished lubricant, particularly the cold crank viscosity, and for this reason are not normally used. In addition, they are more difficult to react with MA due to their higher viscosity.

3.4 Dispersant Basicity

The amount of polyamines added to the PIBSA will determine the basicity of the dispersant. This is referred to as total base number (TBN) and is measured by the ASTM D-2896 method. The units of measurement for TBN are mg KOH/g. The TBN of the dispersant will give a good indication of the dispersant structure. Higher levels of polyamines, i.e., more base, will predominantly yield a mono-succinimide structure, which is the most basic of the PIBSA dispersants (see Figure 11). When there is a molar excess of PIB succinic anhydride, more of the bis and tris structures will predominate (see Figure 12).

3.5 Succinate Ester Dispersants

These dispersants are prepared from a PIBSA and a polyol, as shown in Figure 13. Esterbased dispersants are used to reduce sludge and piston deposits and function in a similar fashion to the succinimide-based dispersants.

3.6 Mannich Dispersants

These types of dispersants are prepared by reacting a PIB phenol with a polyamine in the presence of formaldehyde. The resulting dispersant has some antioxidant properties (Figure 14). This family of dispersants is typically used in gasoline engine oils.

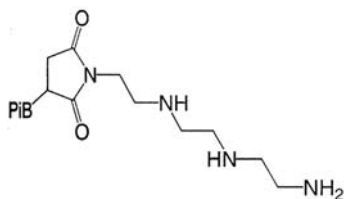


Figure 11 Example of mono-succinimide from TETA (triethylenetetramine).

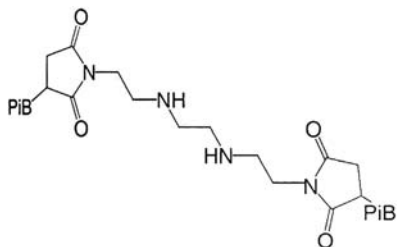


Figure 12 Example of bis-succinimide from TETA.

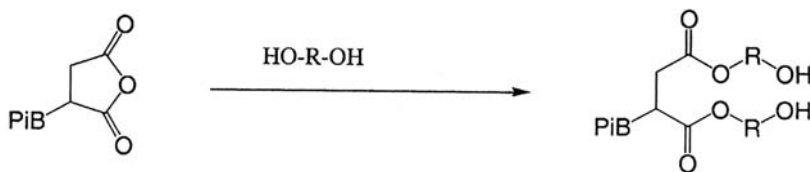


Figure 13 Example of a simple succinate ester dispersant.

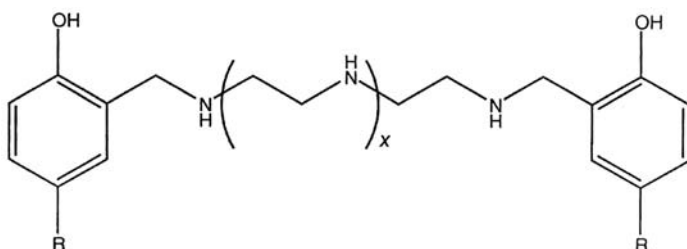


Figure 14 Mannich dispersant.

3.7 Soot Contamination in Diesel Engine Oils

The soot contaminants in heavy-duty diesel engines usually appear when the engine is operating under very high loads or when the fuel injection is retarded (i.e., injected late in the cranking cycle). Under specific engine conditions the small soot particles, typically less than 200 nm, will agglomerate into a larger macrostructure, leading to a significant rise in oil viscosity. The structure of the dispersant is key to the lubricant's ability to minimize these structures from forming. Thus, with the correct choice of dispersant, it is possible to reduce the soot-related viscosity increase and also maintain cleanliness throughout the engine by preventing the large soot structures from settling out.

Over the past 10 to 20 years, the main reason for adding dispersants to diesel engine oils has been the increasing levels of soot, especially in the modern low-emission engines. During the 1990s the level of soot in diesel engine oil increased as a result of new engine technologies designed to reduce NO_x and particulate emissions. This trend accelerated in the United States as older engine designs were changed to meet the U.S. 1990 exhaust emission regulations and then more latterly in Europe during 1992 for the Euro I regulations. During this period, retarded fuel injection was one of the main strategies employed by OEMs to reduce NO_x emissions, resulting in more unburned fuel entering the crankcase oil as soot particles. Combined with extended oil drain intervals, it is not unusual to see soot levels as high as 5% in certain types of duty cycles. This trend is set to continue as more legislation appears on the horizon aimed at reducing diesel exhaust emissions.

One of the most important factors in dispersing soot is the dispersant TBN. Typically, as the base number of the succinimide dispersant increases, the dispersant molecular weight tends to lower values since more of the mono-succinimide structure prevails with more primary nitrogen. This type of dispersant is the most efficient for use in diesel engines, especially modern low-emission engines where there are high

levels of oil soot. The effectiveness of the dispersant is determined by its ability to separate soot particles and thus prevent them from agglomerating. The mechanism whereby this occurs can be represented by the basic dispersant molecule attaching itself to an acidic site on the surface of the soot particle. Assuming that sufficient dispersant molecules are attached to the soot particle, the PIB chains will prevent the soot particles from coming together. The stability of the soot dispersion is influenced by the molecular weight of the PIB and the level of reactive amines (primary and secondary) per molecule of PIB. A very simplistic representation of a soot–dispersant interaction is given in Figure 15. It is fair to say that a lot of energy has been spent finding the most optimum dispersant for dispersing soot, as the patent literature demonstrates. Each individual additive company will have its favored structures.

3.8 Soot-Thickening Tests

As the soot levels of heavy-duty diesel engine oils increased, OEMs, particularly in North America, introduced engine tests to evaluate the oils' ability to disperse soot. One of the tests used to evaluate soot-mediated oil thickening for a low-emission engine was the Mack T-7. This is included into the Mack EO-K and API CF-4 specifications. As the engine technologies progressed to lower emission levels, more severe tests were introduced into API CG-4 and API CH-4 specifications. [Table 1](#) illustrates the progression of the Mack engine tests and the limits applied to the API C categories.

For light-duty diesel applications, Peugeot introduced the XUD-11 soot-thickening test for ACEA passenger car diesel oil approvals. This test, now in its second generation and called the XUD11 BTE, is used to measure oil thickening at soot levels up to 4%. Because the level of soot is much higher compared to what is typically found in European passenger car diesels pre-Euro 2 (1996), the test makes a good measure of the oils' ability to minimize oxidative soot-thickening for small European diesel engines. Criteria have also been applied to the Mercedes OM602A, OM364LA, and OM441LA diesel engine tests regarding soot-related oil thickening

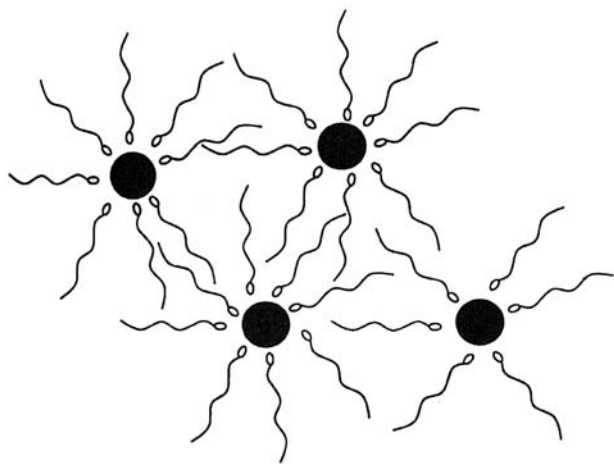


Figure 15 Dispersant – soot interaction.

Table 1 Mack Engine Tests to Evaluate Soot Mediated Oil Thickening

Engine oil category	Engine test	Limits
API CF-4	Mack T-7	≤ 0.4 cSt/hr (last 50 hr of test)
API CG-4	Mack T-8	≤ 11.5 cSt @ 3.8% soot
API CH-4	Mack T-8E	$\leq 2.1 \times$ sheared viscosity* @ 4.8% soot

*Sheared viscosity for Mack T-8E = $(KV_{\text{initial}} + KV_{\text{DIN sheared}})/2$.

and sludge control. Despite all these tests, the engines that have driven oil formulations to ever-higher levels of basic dispersant are still the Mack engines. A comparison of an API CG-4 formulation and an API CH-4 formulation in the Mack T-8 is shown in Figure 16. This demonstrates the progression of dispersant characteristics from API CG-4 to API CH-4.

3.9 Seal Testing

The balance between soot handling and seal compatibility has provided lubricant formulators with significant challenges over the past 10 years, especially as seal testing is a major part of the oil approval process in Europe.

The most difficult issue to contend with is that the highly basic dispersants, used in diesel oil formulations to disperse soot, are aggressive toward fluoroelastomer seals. There are many fluoroelastomer seal tests one common example is the Volkswagen PV3344 test, which is a requirement for Volkswagen oil approvals. There are also seal test requirements for most of the European engine manufacturers, e.g., Mercedes Benz, MAN, and MTU and collectively through ACEA (Association of European Automotive Manufacturers). A comparison of three formulations with different dispersants in a Mercedes Benz seal test is shown in Table 2. This clearly

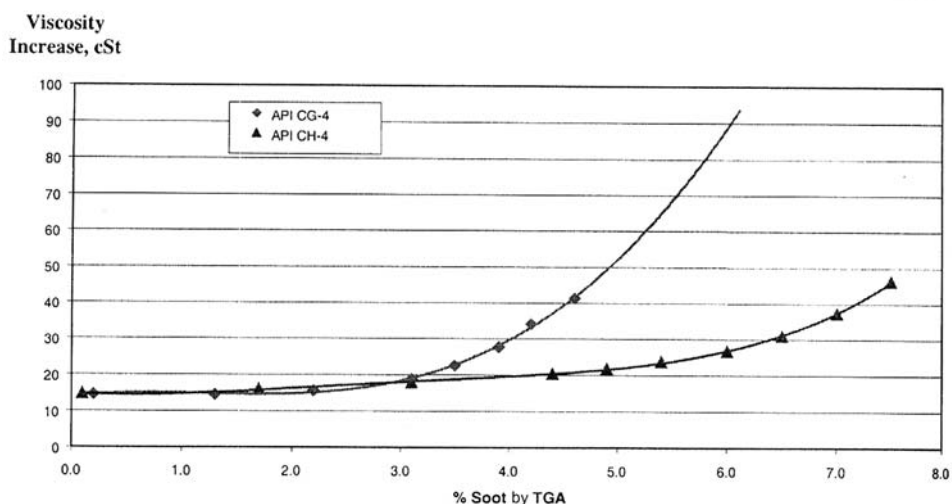


Figure 16 Comparison of an API CG-4 formulation versus an API CH-4 formulation in the Mack T-8 engine test.

shows that as the soot dispersancy is increased for API CH-4, the MB fluoroelastomer seal test worsens.

3.10 Corrosion

Another potential drawback with high-TBN dispersants is that they tend to be more aggressive toward Cu/Pb bearings. This has led some additive companies to treat their dispersants with boron compounds, e.g., boric acid, to reduce Cu/Pb corrosion. In some cases this can improve the antiwear properties, but it usually reduces the effectiveness of the dispersant at dispersing soot. Clearly a balance has to be found and formulators will use different dispersants to meet the various requirements.

3.11 Sludge

Under certain conditions sludge will accumulate in an internal combustion engine. During the 1980s this problem intensified throughout the world, particularly in gasoline engines in Germany, Great Britain, and the United States. The origins of the problem are most likely related to fuel quality, drive cycles, extended oil drain intervals, and the redirection of blow-by gas into the rocker cover. Sludge buildup, if left unchecked, can spread throughout the engine, leading to reduced oil flow through the filter and drain-back holes on the valve deck. In extreme situations this will lead to engine seizure. The problems were not linked to poor-quality lubricants. However, as lubricant technology evolved, it was found that newer lubricant formulations could help alleviate the problem.

Sludges can be split into low-temperature sludges and high-temperature sludges. Sludges formed at low temperatures will tend to be soft and easily removable from surfaces by wiping. As previously mentioned the sludge-forming mechanism is thought to be accelerated by the transfer of blow-by gases into the oil. Blow-by gases contain water, acids, and partially burned hydrocarbons in the form of oxygenates and olefins. The olefins react further with nitrogen oxides to form oil-insoluble products. Fuels with high end boiling points or with high aromatics also tend to contribute to more sludge. Once formed, highway driving will exacerbate the problem as the engine runs hotter, thereby causing the sludge to bake on.

Sludge formation is reduced by the addition of basic succinimide dispersants, particularly the high-molecular-weight types. The addition of boric acid to a

Table 2 Effect of Dispersant TBN on Mercedes-Benz Fluoroelastomer Seals

Formulation Max variation of A K6 Viton	A	B	C
Hardness (Shore A)	-3	0	1
Volume (%)	1	1	0.9
Tensile strength (%)	-8	-32	-46
Elongation rupture (%)	-15	-33	-38
	Pass	Pass	Borderline fail

Key to formulations:

A=European passenger car gasoline/diesel formulation

B=North American heavy-duty diesel formulation (API CG-4)

C=North American heavy-duty diesel formulation (API CH-4)

succinimide dispersant to make a lower-TBN dispersant will reduce the effectiveness of a dispersant in dispersing sludge [7] while this indicates that basic dispersants are required to neutralize sludge precursors, it has been found that very high levels of basic nitrogen are not necessarily required for sludge dispersion in gasoline engines. For Sequence VE performance, high-molecular-weight PIB bis-succinimide dispersants have demonstrated excellent performance. This would appear to indicate that the mechanism of sludge formation in a gasoline engine is different from the agglomeration of soot in a diesel engine, which does require high levels of basic nitrogen especially in low-saturate mineral base stocks. While bis- and mono-succinimide dispersants are used in both gasoline and diesel engine oils, it would be fair to say that more recently, diesel engine oils have tended to higher levels of basic dispersants, with correspondingly higher levels of PIB mono-succinimides compared to gasoline engine oils. One of the big challenges for formulators since API CG-4 has been to develop lubricants that meet the requirements of both gasoline and diesel engine oils, the so-called universal engine oils. This requires careful formulation with both bis- and mono-succinimide dispersants.

When formulating an engine oil, it is also important to consider the interactions between the succinimide dispersant and other additive such as ZDP. A complex between ZDP and succinimide polyamine has been observed in laboratory tests especially where there is a high basic nitrogen-to-ZDP ratio [16]. As the level of basic dispersant is increased, sludge and wear will improve. Above a critical concentration of dispersant, the antiwear properties of the ZDP will be dramatically reduced as the basic nitrogen forms a stable complex with the ZDP, effectively reducing its antiwear capability. It has been demonstrated that the ZDP-amine complex retards the rate of peroxide decomposition by ZDP [8], which in turn accelerates the formation of sludge. Sludge will usually increase in line with wear, so clearly a high level of ZDP with a sufficient dispersant level to disperse the sludge is required. High levels of ZDP permit high levels of dispersant to be used in the lubricant, thereby giving superior engine sludge and wear performance. However, phosphorous has been implicated in exhaust catalyst poisoning. Because of this a maximum phosphorous limit of 0.1% weight in the lubricant has been applied to recent API and ILSAC specifications. This means that where phosphorous limits are imposed for API SJ and ILSAC GF-3 lubricants, careful choice of dispersant and ZDP is required. The phosphorous limits are set to be reduced further for ILSAC GF-4, thereby providing more challenges for the lubricant to meet the sludge and wear requirements in future engines.

3.12 Sludge Engine Tests

Although sludge tests have been around for many years, the most significant lubricant tests to address the sludge problems during the 1980s and 1990s were the Sequence VE and Mercedes M102E. More recently the Sequence VG and the MB M111E have superseded these tests and have become the current benchmarks for measuring lubricant sludge-handling performance in Europe and North America. [Table 3](#) lists the test conditions for the various gasoline sludge tests. Sequences IIIE and IIIF are also included since high-temperature sludge is a rated parameter in these gasoline engine tests.

High-temperature sludges are also present in diesel engines and are a rated parameter for several engine tests, particularly the Cummins M11 for API CH-4. Dispersants based on high-molecular-weight PIB are essential in minimizing sludge

Table 3 Sludge Engine Test Comparison

Test	Cylinder config.	Disp. (cc)	Test duration (hr)	Test operation	Duration (hr)	Speed (rpm)	Power (kW)	Coolant temp. (°C)	Oil temp. (°C)	Fuel type
Sequence IIIE (Buick)	V-6	3800	64	steady speed	64	3000	50.6	115	149	Philips GMR leaded gasoline
Sequence IIIF (Buick)	V-6	3800	80	steady speed	80	3600	75.0	115	155	Howell EEE unleaded
Sequence VE (Ford)	I.L.-4 Slider follower	2290	288	Cyclic	2.00	2500	25.0	51.7	68.3	Philips J unleaded gasoline
					1.25	2500	25.0	85.0	98.9	
					0.75	750	0.75	46.1	46.1	
Sequence VG (Ford)	V-8 Roller Follower	4600	216	Cyclic	2	1200	69 kPa	57	68	Unlead gasoline
					1.25	2900	66 kpa	85	100	
					0.75	700	record	45	45	
Mercedes Benz M-111E Sludge	I.L.-4	1998	224	Cyclin	48-hr cold 75-hr WOT 100-hr cyclic	Idle to 5500	Idle to max.	40 to 98	45 to 130	CEC RF-86-T-94 (ULG)
Nissan VG-20E		2000	200	Cyclic	200	800 to 3500	2–9 kgf-m	38 to 100	50–117	Unlead gasoline
Toyota 1G-FE		2000	48	Steady speed	48	4800	6 kgf-m	120	149	Unlead gasoline

buildup in this test. Sludge is also a rated parameter for the Mercedes Benz OM364LA and OM441LA engine tests, although it is not as critical a parameter as the Cummins M11 engine test.

4 ANTIWEAR

4.1 Introduction

As the power of engines has risen, the need for additives to prevent wear has become more important. Initially engines were lightly loaded and could withstand the loading on the bearings and valve train. Corrosive protection of bearing metals was one of the early requirements for engine oils. Fortunately, the additives used to protect bearings usually had mild antiwear properties. These antiwear agents were compounds such as lead salts of long-chain carboxylic acids and were often used in combination with sulfur-containing materials. Oil-soluble sulfur-phosphorous and chlorinated compounds also worked well as antiwear agents. However, the most important advance in antiwear chemistry was made during the 1930s and 1940s with the discovery of zinc dialkyldithiophosphates (ZDDP) [20,32,33]. These compounds were initially used to prevent bearing corrosion but were later found to have exceptional antioxidant and antiwear properties. The antioxidant mechanism of the ZDDP was the key to its ability to reduce bearing corrosion. Since the ZDDP suppresses the formation of peroxides, it prevents the corrosion of Cu/Pb bearings by organic acids.

4.2 Wear Mechanisms

Antiwear additives minimize wear in a mixed or partial lubricant film operating under boundary conditions (Figure 17). A classic example of boundary lubrication is in a nonconforming contact such as a cam on a follower. The partial lubricant film is most likely to occur when the oil is not sufficiently viscous enough to separate the two surfaces completely.

The tendency to boundary lubrication increases as the temperature rises due to the viscosity-temperature dependence of the lubricant. Low contact speeds, high contact pressures, and rough surfaces will also contribute to more boundary lubrication. If these circumstances are taken to the extreme and minimal or no lubricant film exists, then the maximum surface contact will exist (Figure 18). This is defined as an extreme-pressure (EP) contact and is usually associated with very high temperatures and loads. Additives that prevent wear in an EP contact typically require higher activation temperatures and load than an antiwear additive.

Antiwear and EP additives function by thermally decomposing to yield compounds that react with the metal surface. These surface-active compounds form a thin layer that preferentially shears under boundary lubrication conditions.

After the discovery of ZDDP, it rapidly became the most widespread antiwear additive used in lubricants. As a result, many interesting studies have been undertaken on ZDDP with many mechanisms proposed for the antiwear and antioxidant action [10,13,14,17,18]. The performance of the ZDDP is strongly influenced by the decomposition pathways. These pathways are thermolysis, oxidation, and hydrolysis, which in turn depends on the conditions under which the ZDDP is working. In general, it can safely be assumed that the degradation products of the ZDDP form a film on the metal surface, typically rich in phosphorus and oxygen and possibly

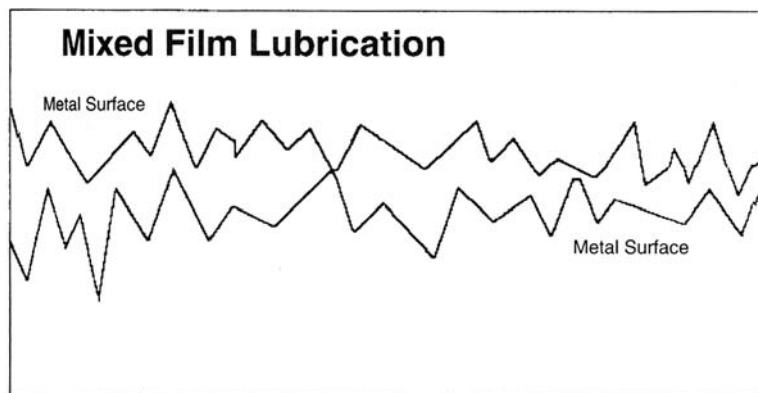


Figure 17 Mixed-film lubrication.

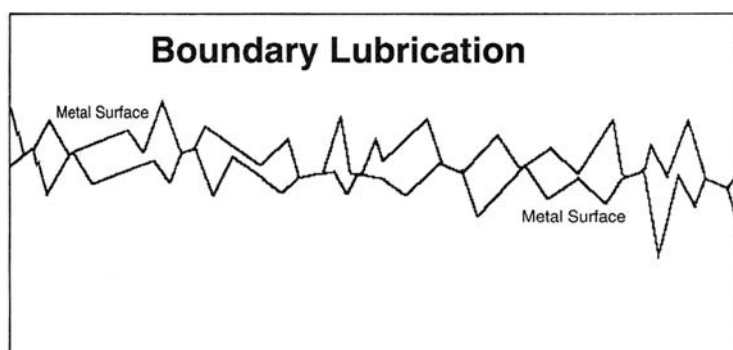
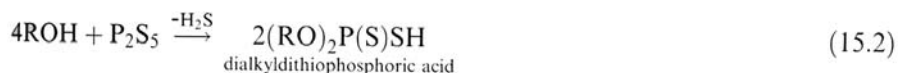


Figure 18 Boundary lubrication.

polymeric. As mentioned above, this layer preferentially shears under boundary lubrication, thus reducing the wear on the metal surfaces. As this layer needs to be constantly replenished, the concentration of ZDDP in the lubricant is critical. It is, therefore, not unusual to find up to 2% wt of ZDDP in a modern lubricant. This equates to a maximum level of about 0.15% phosphorous in the lubricant.

4.3 ZDDP Preparation

ZDDP is prepared by reacting a dialkyldithiophosphoric acid with zinc oxide. The first stage of the process involves the preparation of the acid. The acid is prepared from an alcohol and phosphorous pentasulfide:

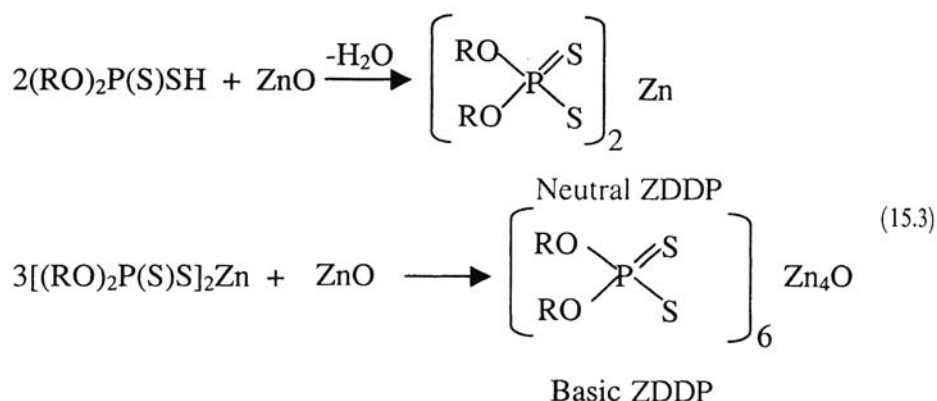


The acid is then neutralized with zinc oxide to yield a ZDDP at around 70–90°C. There are two types of ZDDP structure, neutral and basic, both of which can be observed by ^{13}P NMR. The basic salt is observed at 104 ppm with the neutral salt at 101 ppm. The neutral salt exists as an equilibrium mixture of monomer,

Table 4 Comparison of ZDDP Types in Sequence VE Wear Test

Alcohol type	%Zn as ZDDP	Sequence VE Wear	
		Average (μm)	Maximum (μm)
Mixed C ₃ secondary C ₈ primary	0.127	36	203
C ₈ primary	0.124	121	495

dimmer, and oligomers. The basic salt consists of a central oxygen atom surrounded tetrahedrally by four zinc atoms and six dithiophosphate groups attached symmetrically to the six edges of the tetrahedron. In most industrial processes the ZDDP is left slightly basic for improved stability.



4.4 ZDDP Degradation Mechanisms

The type of alcohol used to prepare the ZDDP determines its thermal and oxidative stability. The most reactive ZDDPs are derived from secondary alcohols and especially those that are lower in molecular weight. Solubility is a limiting factor at carbon numbers less than five; therefore, most ZDDPs will use alcohols with carbon numbers greater than five. Alcohols with a lower carbon number may be used if they are combined with a higher alcohol during the synthesis.

The type of alcohol used in the preparation will have a significant effect on the stability. In most cases the thermal stability of the ZDDP is as follows:

Aryl > primary alkyl > secondary alkyl

The least stable ZDDPs tend to provide improved wear at lower engine oil temperatures. Therefore, the following applies for antiwear action:

Secondary alkyl > primary alkyl > aryl

Tables 4, 5, and 6 indicate the performance of various ZDDPs in a range of gasoline engine wear tests.

The mechanism by which secondary alcohol ZDDPs thermally degrade is shown in Figure 19. The degradation mechanism proceeds rapidly as the

Table 5 Comparison of ZDDP Types is Sequence VD Wear test

Alcohol type	%Zn as ZDDP	Sequence VD Wear
		Average (μm)
C ₆ secondary	0.13	18
Mixed	0.13	48
C ₆ secondary		
C ₈ primary		

Table 6 Comparison of ZDDP Types is Sequence IIID Wear Test

Alcohol type	%Zn as ZDDP	Sequence IIID Wear
		Average (μm)
Mixed	0.13	25
C ₆ secondary		
C ₈ primary		
C ₈ primary	0.13	175

temperature rises and is made easier as a hydrogen on the β position readily leaves to form the alkene. This mechanism may explain why the secondary ZDDPs are much more active antiwear agents particularly at lower temperatures.

In contrast, the primary alcohol ZDDPs are more stable due to the absence of a tertiary hydrogen on the β carbon and therefore more useful for higher-temperature operation and wear such as that found in diesel engines. The mechanism of thermal degradation is via sequential alkyl transfers and relies on an intermolecular alkyl transfer (Figure 20).

4.5 Sequential Alkyl Transfers (Primary ZDDP)

Other additives will affect the rate of thermal degradation of the ZDDP. For instance, it is known that succinimide dispersants will complex with the ZDDP, making it more resistant to thermal degradation. It is, therefore, important to recognize this when formulating an oil additive. Too much dispersant may tie up the ZDDP,

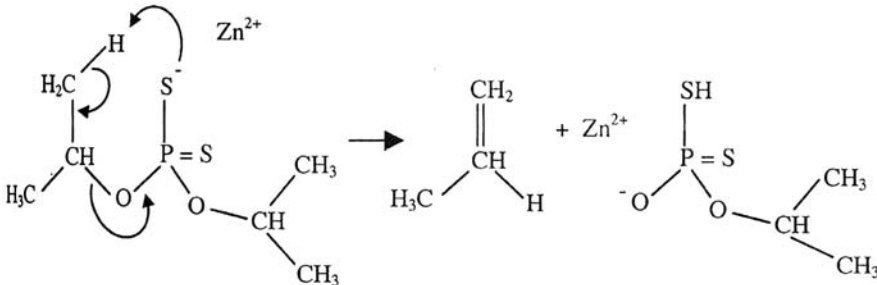


Figure 19 β -elimination (secondary ZDDP).

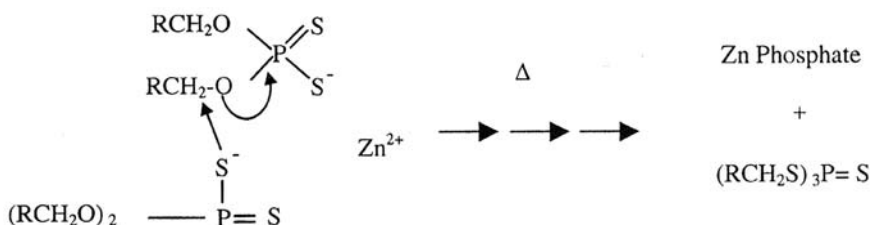


Figure 20 Sequential alkyl transfers (primary ZDDP).

leaving it unable to form an effective antiwear film. A balance has to be found that is dependent on the ZDDP type and the dispersant structure.

As well as thermal degradation pathways for the ZDDP it also degrades at lower temperatures, by oxidation ($<100^\circ\text{C}$), yielding compounds that are beneficial antiwear agents (see Figure 21). This leads to the mechanism of oxidative inhibition by zinc dialkylthiophosphates, which occurs via the above thiophosphoryl disulfide intermediate (see Figure 22). A more detailed mechanism of the antioxidant function of the thiophosphoryl disulfide intermediate is given in Figure 23.

The effectiveness of ZDDP in decomposing hydroperoxides has been linked to wear rates in a motored engine test [15]. Secondary ZDDPs were better at decomposing peroxides than their primary counterparts. A plethora of papers exists in the literature with detailed analyses of the various degradation pathways for the ZDDP molecule and its subsequent effect on the wear and oxidation properties of the lubricant [9–13]. While these give an excellent insight into the ZDDP degradation mechanisms, it must be remembered that the degradation pathways are strongly dependent on the test conditions, i.e., temperature, amount and type of oxidants, etc.

4.6 Antiwear Tests

The Sequence VE and Sequence IV-A gasoline engine tests (for API SJ and ILSAC GF-3, respectively) are designed to test the ability of a lubricant to prevent low-temperature sliding wear in the valve train of a gasoline engine. Secondary ZDDPs will usually perform better than primary ZDDPs in both tests. However, there are certain cases where it is possible to achieve a passing test result with primary ZDDP especially with formulations where a low level of detergent is present. High-temperature gasoline wear is measured in the Sequence IIIE and Peugeot TU3 scuffing test and responds well to most types of ZDDP.

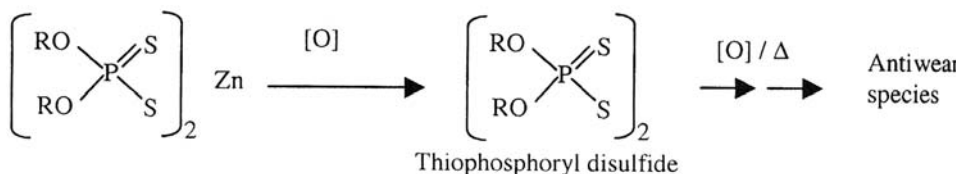


Figure 21 Thiophosphoryl disulfide formation ($[\text{O}]$ can be almost any oxidant such as O_2 , ROOH , H_2O_2 , $\text{Cu}_2\% \text{NO}_x$, etc.)

Table 7 Diesel Wear Tests

Engine test	Specification	Wear measured
GM roller Follower Wear Test	API CG-4,CH-4	Roller follower wear
Cummins M11	API CH-4	Valve bridge wear
Mercedes OM602A	MB Sheet 228.X, 229.X	Cam nose wear
	ACEA B and E sequences	Cylinder wear
Mitsubishi 4D34T	Global DHD-1, JASO DH-1	Cam nose wear

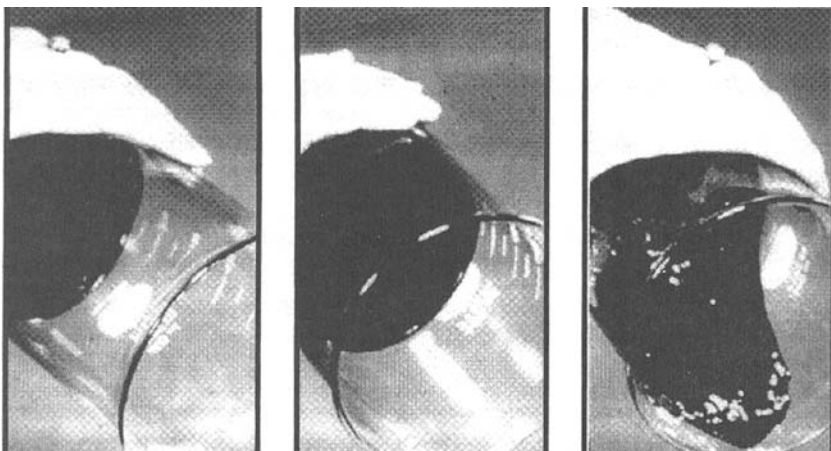
5 ANTIOXIDANTS

5.1 Introduction

Most lubricants, by virtue of being hydrocarbon-based, are susceptible to oxidation [21,22]. If oxidation is not controlled, lubricant decomposition will lead to oil thickening, sludge formation, and the formation of varnish, resin, and corrosive acids [23,25].

The oxidation reactions that occur in a lubricant at elevated temperatures in the presence of atmospheric oxygen may lead to declined lubricant performance such as significant increase in kinematic viscosity observed in severe service conditions or during extended drain intervals (Figure 24).

In general, all types of base oils require addition of antioxidants depending on the amount of unsaturation and “natural inhibition” present. The refined mineral base oils contain “natural inhibitors” in the form of sulfur and nitrogen compounds sufficient for many applications. The oxidative stability of such oils shows a distinct, relatively long induction period. On the other hand, hydrofined oils do not contain these natural inhibitors or contain them only in small quantities. Besides the sulfur and nitrogen compounds, other compounds such as aromatics or partially

**Figure 24** Antioxidants can prevent premature oil thickening.

hydrogenated aromatics and phenolic oxidation products can be of importance; their inhibiting effect is lost during various refining processes. Traditional mineral oils, such as Groups I and II base stocks, show moderate oxidative resistance. Synthetic oils such as polyol esters and hydrogenated poly-alphaolefins (PAOs) exhibit the highest oxidative stability due to their low unsaturated content. The most unstable oils include high unsaturated vegetable triglycerides, such as corn, sunflower, canola, peanut oils, etc.

An overall scheme of lubricant oxidation starts with the conversion of hydrocarbon substrates to carbonyl compounds (Figure 25). Coupling of these polar compounds through Aldol and related reactions builds molecular weight. Eventually, at very high molecular weight (i.e., >1000) the oil is converted to insoluble sludge, which can precipitate on the engine hardware.

5.2 Mechanism of Oxidation of Lubricating Oils

The oxidation of petroleum hydrocarbons proceeds according to a radical chain mechanism via alkyl and peroxy radicals in three stages [25].

5.2.1 Initiation



The initiation step starts by the slow abstraction of a hydrocarbon proton by molecular oxygen to form alkyl- and hydroperoxy-free radicals. This process is also referred to as “auto-oxidation” and is favored by time, higher temperature, and transition metal (i.e., iron, nickel, copper, etc.) catalysis.

5.2.2 Propagation

Propagation starts by the rapid reaction of more oxygen with an alkyl-free radical to form an alkyl peroxy radical, which is also capable of hydrocarbon abstraction to

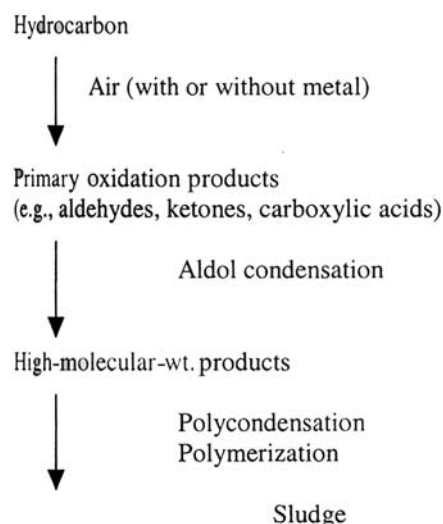


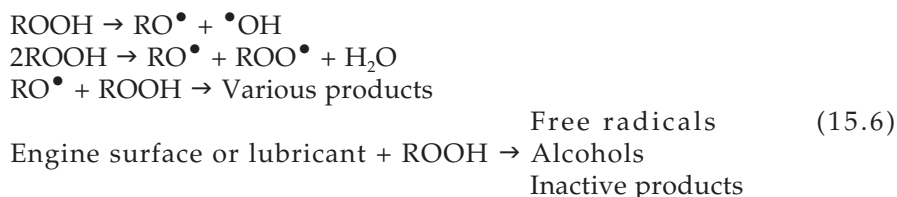
Figure 25 Degradation of mineral oils.

form a hydroperoxide and another alkyl radical. The alkyl radical then may react with more oxygen, starting the chain over [23].



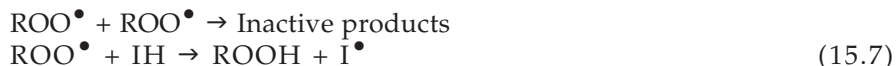
5.2.3 Peroxide Decomposition

Alkyl hydroperoxides are quite reactive and may decompose, especially at higher temperature, to form additional radical species. These can undergo further abstraction and chain propagation reactions, which increase the overall oxidation process. Alkyl peroxides and alkyl peroxy radicals also decompose to neutral oxidation products such as alcohols, aldehydes, ketones, and carboxylic acids. Hydroperoxide decomposition to neutral oxidation products can be viewed as a chain termination step, since free additional radicals are not formed.



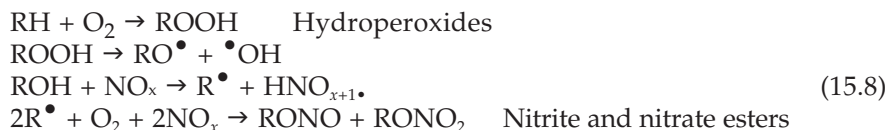
5.2.4 Termination (Self- and Chain Breaking)

During termination stage, the radicals either self-terminate or terminate by reacting with oxidation inhibitors [21].



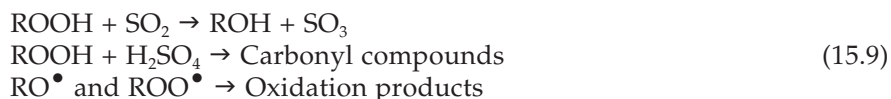
Alternative oxidation pathways are listed below.

5.2.5 Radical Formation



Nitrogen oxides can react with alcohols (an oxidation product) to form alkyl-free radicals, which react with NO_x and oxygen to form nitrate and nitrate ester oxidation products.

5.2.6 Decomposition and Rearrangement



The action of sulfur dioxide and H_2SO_4 (from SO_3 + water) on alkyl hydroperoxides also leads to neutral oxidation products such as alcohols and carbonyl compounds. Aldehydes and ketones can react further and form polymers. Carboxylic acids can attack metallic hardware: rings, valve train, and bearings, leading to extensive wear. Furthermore, they can form metal carboxylates, which further increase the oxidation rate. Wear metals can also enhance the rate of oxidation [24].

5.3 Oxidation Inhibitors

Oxidation inhibitors can be classified in the following matter:

1. Radical scavengers:
nitrogen-containing inhibitors: aryl amines
oxygen-containing inhibitors: phenols
zinc dialkyldithiophosphates (ZDDPs)
2. Hydroperoxide decomposers:
sulfur-containing inhibitors: sulfides, dithiocarbamates, sulfurized olefins
phosphorous-containing inhibitors: phosphates, zinc dialkyldithiophosphates (ZDDPs)

Note that ZDDPs function by both antioxidant mechanisms in addition to providing antiwear protection (covered in the earlier section). This dual (or tri-) functional ability of ZDDPs to provide antiwear performance and antioxidancy by two different pathways explains why these additives are by far the most effective inhibitors, especially on a cost-performance basis.

Phenols or amines of specific structures function as radical acceptors by transfer of a hydrogen atom from the oxygen or nitrogen atom to the hydrocarbon or peroxy radical. The inhibitor radicals thus formed react through radical combination or electron transfer to give ionic compounds, or by addition reactions or formation of complexes that do not maintain the radical chain mechanism of the auto-oxidation reaction. In further reactions very often ethers, betones, or polyaromatic systems, etc. are formed.

5.4 Hindered Phenols and Arylamines

Hindered phenols and arylamines are two prominent examples of inhibitors that act as radical scavengers through hydrogen transfer. [Figure 26](#) illustrates the mechanism of phenol performance.

Among various types of phenols, polyalkylphenols have significant performance advantages over nonalkylated compounds ([Figure 27](#)). The effect of substituents demonstrates the role of electron density and steric hindrance at the phenolic oxygen; an increase in number of alkyl radicals and introduction of electron donors in the o- and p-positions increase the efficiency; the introduction of electron acceptors reduces it. Alpha-branching of alkyl groups in o-position or increasing the alkyl group to C4 in p-position has a beneficial effect [24].

A new type of antioxidant involves the base-catalyzed addition of hindered phenol to Michael acceptors such as acrylate esters. Although more expensive than simple alkylphenols, the originators of this chemistry claim improved upper piston deposits control in certain diesel engine tests and better seal compatibility than arylamines.

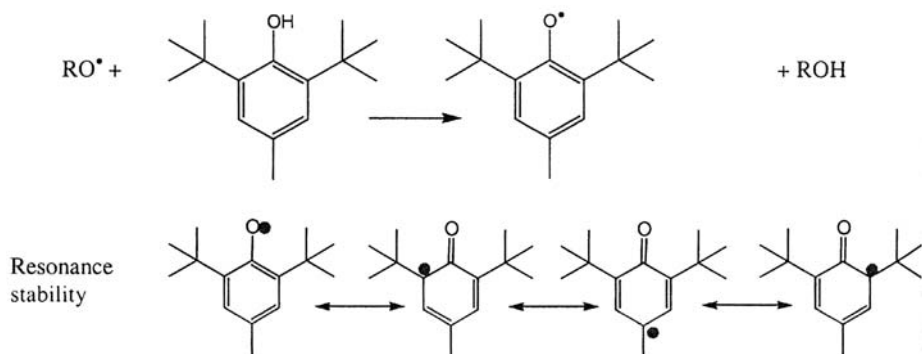


Figure 26 Mechanism of inhibition by hindered phenols.

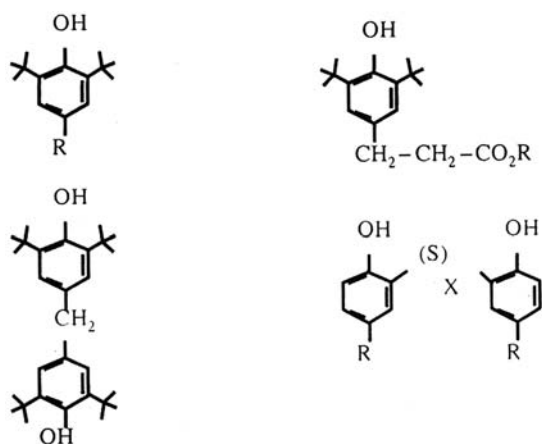


Figure 27 Major types of phenolic antioxidants.

S-coupled ($X = 1,2$) alkylphenols combine the antioxidant benefits of the phenol and sulfide groups.

The mechanism of oxidation inhibition (based on generation of nitrogen radicals) by arylamines is presented in [Figure 28](#).

In general, the alkylated arylamines are more effective antioxidants than alkylphenols because they are

Able to trap more equivalents of radicals: four versus two

Able to better stabilize nitrogen or nitroxyl radicals (by two aryl rings instead of one)

Able to operate at both a low- and high-temperature mechanism (the latter of which regenerate the alkylated arylamine)

Oil-soluble amines such as diphenylamine, phenyl- α -naphthylamine, etc. are the most common type of amine antioxidants used in lubricants. Diphenylamine can be alkylated with aluminum chloride catalyst and a mixture of branched nonene

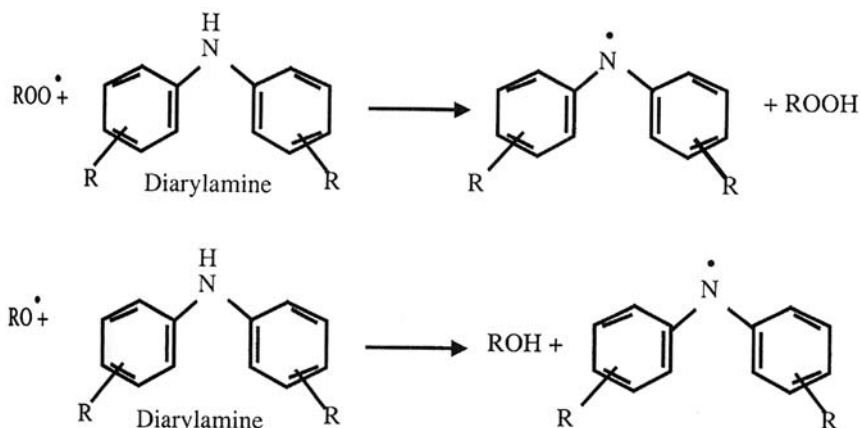


Figure 28 Mechanism of inhibition by arylamines.

olefins. A mixture of mono- and di-alkylate (Figure 29) is intentionally targeted by the reactant charge ratio to produce a liquid product. Diphenylamine is particularly suited for applications at elevated temperatures. Therefore, it is often used to lubricate supersonic aircraft engines and bearings. In these applications, arylamines prevent sludge formation in synthetic ester oils.

5.5 S- and P-Containing Antioxidants

Sulfur, phosphorus, and compounds containing both elements decompose peroxides by reducing the hydroperoxide in the radical chain to alcohols; the sulfur or phosphorus atoms are correspondingly oxidized (Figure 30). Bivalent sulfur compounds (sulfides, etc.) yield sulfoxides and sulfones; trivalent phosphorus compounds (phosphates) are transformed into pentavalent ones (phosphates). Organic compounds of tetravalent sulfur act as peroxide decomposers, but the corresponding hexavalent, in

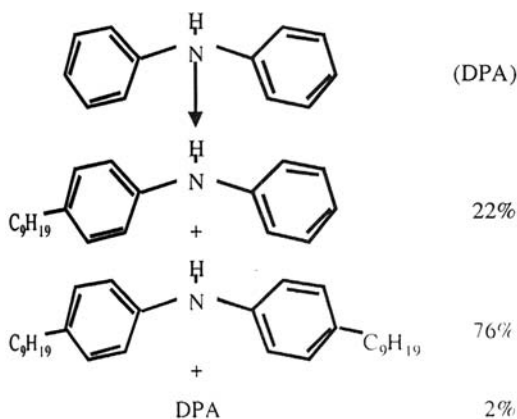


Figure 29 Alkyl aromatic amine as antioxidant.

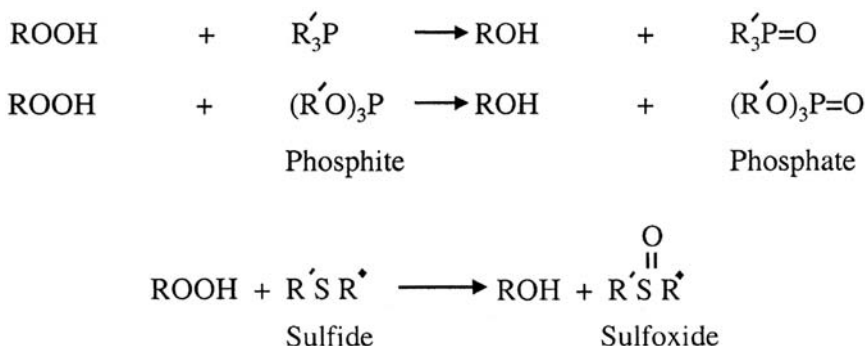


Figure 30 Mechanism of S- and P-containing antioxidants.

line with theory, do not. Destruction of hydroperoxides is important so that these intermediates do not decompose into radicals, which can continue the chain oxidation process.

Phosphates are somewhat hydrolytically unstable, and due to limits on phosphorus level in crankcase oils, these additives are generally limited to application in gear lubricants. ZDDPs are more efficient phosphorous containing auto-oxidants for crankcase oils, with the added benefit of antiwear performance.

ZDDPs convert hydroperoxides to one equivalent of an alcohol and a carbonyl compound (Figure 31). The ZDDP is regenerated intact and available to convert another hydroperoxide molecule. Many cycles of hydroperoxide decomposition are carried out by the ZDDP, prior to its eventual breakdown.

5.6 Sulfur Compounds

Elemental sulfur is an efficient oxidation inhibitor; however, it shows a strong corrosion tendency.

From the practical approach, numerous dialkyl sulfides and polysulfides, diaryl sulfides, modified thiols, mercaptobenzimidazoles, thiophene derivatives, xanthogenates, zinc dialkyldithiocarbamates, thioglycols, thioaldehydes, and others have been examined as inhibitors. Dibenzyl disulfide must be mentioned among the alkyaromatic S compounds.

Alkylphenol sulfides, which are formed in the reaction of alkylphenols such as butyl-, amyl-, or octylphenol with sulfur chloride, are more active than the compounds of the dibenzyl disulfide type, due to the position of the sulfur next to the OH group.

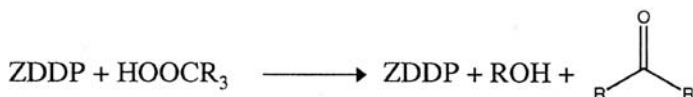


Figure 31 ZDDPS hydroperoxide destruction.

Modern compounds of this type contain mostly tert-butyl radicals besides the methyl groups, as, for instance, 4,4'-thio-bis-(2-tert-butyl)-5-methylphenol. Sulfur-nitrogen compounds are also suited as oxidation inhibitors for lubricating oils (2-mercaptobenzimidazole, mercaptotriazines, reaction products of benzotriazole-alkylvinyl ethers or esters, phenothiazine and its alkyl derivatives). Among the sulfur-containing carboxylic acid esters, 3,3'-thio-bis-(propionic-acid dodecyl ester) and bis-(3,5-di-tert-butyl-4-hydroxybenzyl)-malonic acid-bis-(3-thia-pentadecyl) ester have been applied with success. These compounds have been replaced by the dialkyl-dithiophosphates due to their broad application spectrum. Sulfoxides, sometimes in combination with aromatic amines, have also been utilized.

5.7 Phosphorous Compounds

Red phosphorus possesses oxidation-inhibiting properties but cannot be used because of its corrosivity toward nonferrous metals and alloys. Triaryl and trialkyl phosphates have been proposed as thermally stable inhibitors; however, their applications are limited. Combined phosphoric acid-phenol derivatives such as 3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid dialkyl esters or phosphonic acid piperazides have a better effect.

5.8 Sulfur-Phosphorus Compounds

Today metal salts of thiophosphoric acids are used predominantly as oxidation inhibitors for crankcase oils. In principle, compounds that contain sulfur and phosphorus are significantly more efficient than inhibitors that contain only sulfur or phosphorus. Most widely used are the zinc dialkyldithiophosphates, which are prepared by the reaction of P_2S_5 with the respective higher alcohols (e.g., hexyl, 2-ethylhexyl, octyl alcohols), followed by the reaction with zinc oxide. The temperature of the exothermic salt formation is kept at 20°C by successive addition of the zinc oxide and cooling and is limited even at the end of the reaction to 80°C because of the thermal ability of the free dialkyldithiophosphoric acids. They react very corrosively with metals and are toxic. Metal dialkyldithiophosphates are prepared in mineral oil solution. Their solubility in hydrocarbon oils increased with the increasing number of carbon atoms of the alkyl residues and is satisfactory with the diamyl compounds and higher. Longer-chain derivatives act as solubilizers for short-chain products. Metal dialkyldithiophosphates act not only as antioxidants, but also as corrosion inhibitors and extreme-pressure additives.

The efficiency of Zn dialkyldithiophosphates (with octyl or cetyl and, respectively, propyl, butyl, or octyl radicals in various combinations) decreased with increasing molecular mass of the alcohol substituents. The best results have been obtained with isopropyl and isoamyl radicals.

Reaction products of P_2S_5 with terpenes (dipentene, -pentene), polybutenes, olefins, and unsaturated esters belong to the same group; among these, the terpene and polybutene products have been proposed for crankcase oils. Metal dialkyldithiophosphates serve at the same time as detergents, extreme-pressure additives, and anticorrosion agents, when the corrosion is caused by oxidation products; in this case the metal is protected from attack by organic acids by the formation of sulfide or phosphate films. 2,5-Dimercaptothiadiazole derivatives have a similar effect.

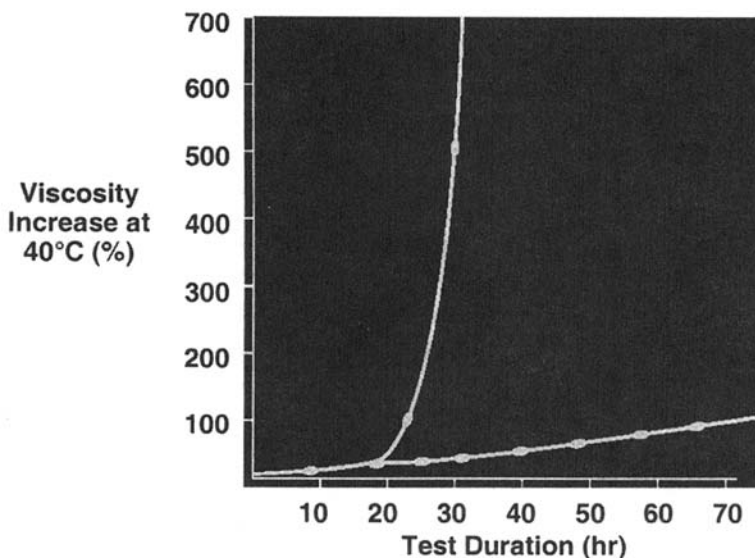
Table 8 Approximate Temperature of Internal Surfaces in a V-8 Engine

Area of engine	Temperature range (°C)
Exhaust valve head	650–730
Exhaust valve stem	635–675
Combustion chamber gases	2300–2500
Combustion chamber wall	204–260
Piston crown	204–426
Piston rings	149–315
Piston (wrist) pin	120–230
Piston skirt	93–204
Top cylinder wall	93–371
Bottom cylinder wall	Up to 149
Main bearings	Up to 177
Connecting rod bearings	93–204

5.9 Antioxidant Selection, Synergism, and Testing

Most crankcase engine antioxidant needs are met by the ZDDP. Today's higher-temperature engines (Table 8) require supplemental ashless antioxidants to pass the Sequence IIIE engine. Therefore, modern engine oils use three or more different types of antioxidants, with the highest level (0.1 to 0.15% wt) being the ZDDP.

An example of antioxidant effectiveness is shown in Figure 32. The Previous-generation engine to measure lubricant oxidation was the Sequence IIID, which required a maximum oil kinematic viscosity increase of 375 cSt @ 80 hr of operation. A fail result is shown for the base formulation at less than halfway through.

**Figure 32** Oxidative viscosity control by arylamine in a Sequence IIID test. (From Ref. 27.)

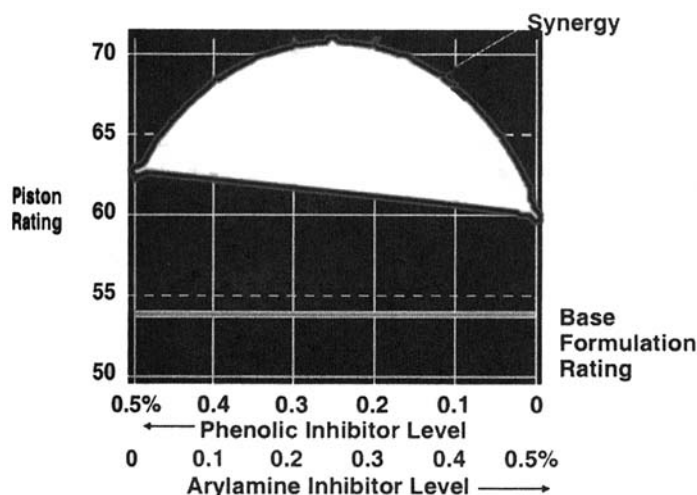


Figure 33 Synergism between a phenol and an arylamine in controlling deposits (MWM-B Engine). (From Ref. 27.)

the test (30 hr). Addition of 0.5% wt arylamine antioxidant to base formulation results in easily meeting the kinematic viscosity increase requirement. The same pass result could be obtained by increasing the ZDDP level, but the current limits on phosphorous level prevent this option.

Another important antioxidant phenomenon is known as inhibitor synergism. Another way of stating the definition shown here is, “[Half] (or partial) levels of two compounds produces a greater benefit than a full level of either alone.” Synergistic combinations of inhibitors can extend a lubricant’s temperature and use ranges, thereby boosting its performance. An example of the synergism between alkylphenol and amine inhibitors is shown in Figure 33. A graphic example of antioxidant synergism is shown the figure for European MWM-B diesel engine test. A perfect piston rating (clean surface) is 100, with a passing limit set at 65.

Either formulations containing 0.5% wt of alkylphenol (rating = 63) or 0.5% wt of arylamine as inhibitor (rating = 60) alone do not provide a sufficient deposit control to pass this test. However, a mixture of two inhibitors at 0.25% wt each did offer an outstanding rating, 71, which is a pass result.

The efficiency of antioxidants in lubricating oils is tested on the laboratory scale in a battery of bench tests and engine tests under more severe conditions. This is particularly true for motor oils, where only the practical test in the engine can assess, for instance, the high-temperature efficiency of dithiophosphates and the frequently antagonistic effects of dispersants and oxidation inhibitors in a given additive combination.

As a rule, however, the final formulations of products are subjected to time-consuming field testing. Here are some screen and engine oxidation performance tests.

The ASTM D-943, or Turbine Oil Oxidation, test is used for hydraulic oils. In this screen, molecular oxygen is blown through a quart of the oil at 95°C

containing an iron and copper oil. The hours to reach an oil TAN of 2.0 are recorded, with a pass result considered to be anywhere from 1000 to 3000 hr, depending on the specific customer approval.

The ASTM D-2272 (RBOT = Rotary Bomb Oxidation test) and ASTM D-4742 (TFOUT = Thin Film Oxygen Uptake test) are two other industry-recognized bench tests. These screens use pressure to accelerate the oxidation process to simulate the lubricant’s extended service or “real-world” conditions. The RBOT also finds utility for formulating industrial oils, while the TFOUT is used to measure the oxidation performance of passenger car and heavy-duty diesel engine oils.

ISOT (Indiana Stirred Oxidation test) has several versions, with temperature ranging from 150–165°C. The beaker of oil is stirred vigorously for 24 hours in presence of iron and copper catalysts. Measurements include the oil’s kinematic viscosity increase, TAN built up, and amount of pentane insoluble sludge generated.

PDSC (Pressure Differential Scanning of Calorimetry) is designed to predict the improvement inhibitors add to an oil of poor oxidative stability.

Passenger car motor oils (PCMO) engines for oxidation performance consist of

The Sequence IIIE and Sequence IIIF to measure an oil’s viscosity built up
The Sequence VE and Sequence VG to measure sludge control (Table 3)

The extreme temperature ranges reached in the Sequence VE engine are given in Table 8. The oil bulk temperature does not reach these high temperatures, but the fluid operates in close proximity of these parts. Since the oxidation process is accelerated by temperature, one can see why an oil’s antioxidant system must be specially designed to be effective.

Typical passenger engine design has been undergoing dramatic changes since it has been introduced to the public in early 1920s. Table 9 summarizes several major design/fluid system changes observed [34]. The two critical parameters affecting lubricant stability and projected life are:

- 1. The large increase in the engine oil temperature (2 ×)
- 2. While the amount of lubricant has been steadily decreasing (~ 5 ×)

These two factors have put extra demands on the lubricant’s antioxidant system, while somewhat recent limits on phosphorous level have “capped” the used of ZDDP.

Table 9 Changes in the V-8 Engine over Last Seven Decades

	1920	1960	1990
Engine capacity, L	6	2	1.6
Brake horse power	50	70	130
Engine speed, rpm	1200	5000	7000
Oil temperature, °C/°F	60/140	90/194	130/266
Oil capacity, L	14	4.5	3.5
Valve train	Side valves	Push rod, overhead valves	Twin overhead camshafts, 4 valve
Fueling system	Single-choke Carburetor	Multichoke Carburetor	Fuel-injected

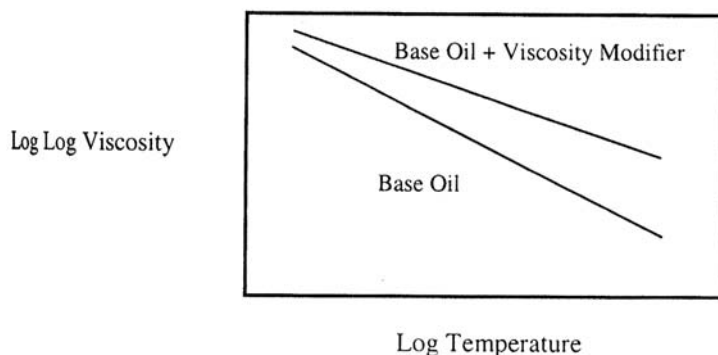


Figure 34 Effect of viscosity modifier on base oil viscosity-temperature dependence.

6 VISCOSITY MODIFIERS

6.1 Introduction

Viscosity modifiers (VMs) are added to a lubricant formulation in order to reduce the viscosity-temperature dependence of the base oils. This class of lubricant additives is the technology that enabled the development of multigrade lubricants in 1960s. The primary feature of multigrades is that they allow the engine to start at low temperatures while providing sufficient viscosity at elevated temperatures to protect the engine against wear.

A lubricant oil formulation based on a Group I mineral base stock without a VM additive will have a limited range of temperature operation since it has a relatively strong viscosity-temperature relationship. Viscosity modifiers are oil-soluble polymers that, when added to a base oil and additive mixture, will thicken the mixture at high temperatures while having a minimal thickening effect at lower temperatures (Figure 34). A very simplified mechanism to explain this phenomenon would be that the polymer-oil interaction at low temperature is minimal but increases as the temperature rises. This interaction of the polymer with the base oil at elevated temperatures increases the effective hydrodynamic volume of the polymer, thereby increasing the effective volume fraction of the VM. This, in turn, leads to an increase in lubricant viscosity. In order to make use of this phenomenon, a low-viscosity base oil mix is used to which is added the VM and additive mixture. The low-viscosity base oils permit the oil to flow freely at low temperatures while the VM will increase the viscosity at higher temperatures.

6.2 Viscosity Modifier Types

Several types of viscosity modifiers are available to the oil formulator. Each of these has strengths and weaknesses. Therefore, it is sensible to select the correct type for the intended application. [Table 10](#) details some of the most common viscosity modifiers in use today.

OCPs are prepared by either Ziegler-Natta or metallocene catalysis. Besides containing ethylene and propylene, diene monomers may be added to improve the

Table 10 Viscosity Modifiers

Viscosity modifier name	Abbreviation	Polymer structure
Olefin copolymer Poly(ethylene/propylene) [may contain diene monomer]	OCP	Linear copolymer, can contain long-chain branching
Polyalkylmethacrylate	PMA	Linear copolymer
Hydrogenated radial polyisoprene, can contain styrene as comonomer	HRI	Star polymer
Hydrogenated styrene-isoprene	HIS	Linear A-B block copolymer
Hydrogenated styrene-butadiene	HSB	Linear tapered block copolymer
Polyisobutylene	PIB	Linear homopolymer
Styrene-ester, alternating copolymer of styrene and alkylmaleate	SE	Linear copolymer

handling characteristics of the solid from of the polymer. The relative amounts of each monomer will dictate the solubility of the copolymer. As the level of ethylene in the copolymer increases, polymer solubility decreases, especially at low temperatures. This effect at low temperatures has the beneficial effect of lowering the polymer contribution to subambient viscosity. But one must be careful not to go too far since at very high-ethylene contents the OCP will drop out of solution or form gels at low temperature. This may only manifest itself after several months' storage at low temperatures. The monomer sequence distribution is also critical and can be carefully controlled to maximize the amount of ethylene in the copolymer and hence give minimal low-temperature thickening. OCPs are the most popular type of VM in use today due to their high thickening efficiency and relatively low cost.

Styrene-diene copolymers are prepared by an anionic polymerization of styrene with either butadiene or isoprene. The residual unsaturation in the backbone is removed by hydrogenation. Tapered block copolymers are prepared by charging both monomers together at the beginning of the reaction. To synthesize A-B block copolymers, the monomers are added sequentially. Anionic polymerization yields polymers with very narrow molecular-weight distributions especially when compared with those of OCPs and PMAs. A narrow molecular-weight distribution yields the maximum shear-stability-to-thickening-efficiency ratio for a linear polymer. Because styrene-diene copolymers also possess excellent low-temperature properties and good thickening efficiency, they have found widespread use in engine oils. One of the few drawbacks is that, relative to OCPs, they are expensive to make due to the two-stage synthesis process and more expensive starting materials. Another issue is that A-B block copolymers undergo more temporary viscosity loss under high-temperature, high-shear-rate conditions (such as in lubricated journal bearings), especially when compared to OCPs.

Star polymers are prepared by an "arms-first" process whereby isoprene (and an optional co-monomer) are anionically polymerized to a predetermined molecular

weight. The “arms” are then linked together by adding divinylbenzene, which forms an ill-defined gel core. The number of arms per star is defined by the amount of divinylbenzene relative to the polymer “arm” concentration. Finally, the star polymer is hydrogenated. These polymers have exceptional low-temperature properties but undergo more permanent viscosity loss under severe operating conditions when compared to OCPs at the same nominal SSI.

PMAs are prepared by free-radical polymerization of alkylmethacrylate monomers. This produces a polymer with a relatively broad molecular-weight distribution. To reduce molecular weight and hence increase shear stability of the polymer, the initiator concentration is increased. In addition, a chain transfer agent may be added during the polymerization process. This stops the polymer chains from growing and enables the production of a polymer with low molecular weight and exceptional shear stability. The composition of the monomers in the polymer backbone is chosen to optimize low-temperature properties, VI, and thickening efficiency. PMAs are frequently used because of their exceptional low-temperature viscometric properties. Because of this they are used extensively as viscosity modifiers in gear oils, automatic-transmission fluids, and hydraulic oils as well as pour point depressants. In recent years, OCPs have gained market share from PMAs in engine oils due to their relatively low cost and acceptable performance. PMAs can also be manufactured with dispersant functionality, which adds another performance attribute to an already highly versatile additive. The most direct method for preparing dispersant PMAs is to incorporate a nitrogen-containing monomer into the polymer during copolymerization. Alternately, various nitrogen-monomer grafting techniques can be used.

6.3 Dispersant Viscosity Modifiers (dVMs)

A variety of VMs can be prepared with the incorporation of dispersant properties. These dVMs have been used to provide improved sludge and soot-handling performance to engine oil lubricants. They can either substitute for or add to the existing dispersant in the formulation. As a replacement for dispersant, they are required to provide equivalent performance. As a top treat to the existing additive they will provide a boost in performance especially in areas of sludge and soot handling. Examples include dispersant PMAs and dispersant OCPs.

6.4 Shear Stability of Engine Oils

Polymeric viscosity modifiers are susceptible to mechanical and in some case thermal shearing, leading to a loss in oil viscosity. The shear stability index (SSI) of an engine oil VM is defined by the following equation. The SSI gives an indication of the mechanical stability of the VM:

$$SSI = \frac{m_i - m_f}{m_f - m_o} \times 100 \quad (15.10)$$

where

m_i = initial viscosity of lubricant with the viscosity modifier, cSt.

m_f = final viscosity of lubricant after shear.*

m_o = viscosity of lubricant without the viscosity modifier, cSt.

Numerically the SSI can be explained as follows: a VM with a low SSI number is more shear-stable while a VM with a high SSI number is less shear-stable. The SSI value of the VM will depend on its molecular weight. Higher-molecular-weight VMs will have the greatest thickening efficiency for a given weight of polymer but will have the lowest shear stability (highest SSI). 55 SSI represents the lowest shear stability acceptable for modern engine oils. While this is not unusual for North American passenger car motor oils, it is quite uncommon to find this shear stability used in Europe, where minimum shear stability is specified in the ACEA and OEM specifications. A VM with 25 SSI or less is typical for European diesel and gasoline applications while a 35 SSI VM or less is preferred for North American diesel formulations.

6.5 Viscosity Grade

A lubricant's viscosity grade, which defines the useful operating temperatures under which it may be used, is defined by a number of viscometric measurements given in the various SAE specifications. Polymeric viscosity modifiers are crucial in allowing the many viscosity grades to be made. Most OEMs will use the viscosity grade to define the lubricant that best works in their equipment. For engine oil lubricants the viscosity grade is defined by the SAE J300 specification, as shown in Table 11.

In general, an OEM will aim to use the lowest-viscosity oil possible, in order to reduce energy losses due to friction. However, it will usually recommend a minimum oil viscosity with which its equipment will work comfortably. These limits may not always coincide with the SAE J300 specification, especially in the case of the high-temperature, high-shear viscosity. European OEMs have historically been more conservative and most have specified a minimum high-temperature, high-shear-rate (HTHS) viscosity of 3.5 cP for their engine oils regardless of viscosity grade. This limit is still applied by European heavy-duty diesel OEMs since bearing wear is seen a critical performance parameter. This would mean that an SAE 10W-30 oil would not only have to meet the SAE viscosity grade but would also have to be greater than 3.5 cP in the HTHS viscosity test. North American diesel oils are similar to their European counterparts with 15W-40 making up the majority of the market. However, there are some of 10W30 oils in use for which there are no HTHS viscosity minimum limits other than that specified in SAE J300.

For some European passenger car OEMs there has been some relaxation in the OEM limits applied to the HTHS viscosity as engine designs have changed to accommodate lower-viscosity oils. Lower-viscosity oils enable improvements in fuel economy to be made. For example, Volkswagen has published oil specifications VW 503 and 506 for its gasoline and diesel engines. These specify an SAE 0W-30 with an HTHS from 2.9–3.4 cP together with a fuel economy target. The reduction in HTHS

**Note that the SSI value depends the particular shearing device used to measure shear stability. Common devices include the Kurt Orbahn fuel injector rig, the CRC L-38 engine test, the sonic shear device, and the KRL tapered bearing rig. The latter is primarily used to measure the SSI of driveline fluids such as highly shear-stable ATF and gear oils.*

Table 11 SAE Viscosity Grades for Engine Oils

SAE viscosity grade	Low-temperature viscosities		High-temperature viscosities		
	Cranking (cP) max at temp, °C	Pumping (cP) max with no yield stress at temp, °C	Kinematic (cSt) at 100°C		High-shear rate (cp) at 150°C min
			Min	Max	
0W	6200 at -35	60,000 at -40	3.8		
5W	6600 at -30	60,000 at -35	3.8		
10W	7000 at -25	60,000 at -30	4.1		
15W	7000 at -20	60,000 at -25	5.6		
20W	9500 at -15	60,000 at -20	5.6		
25W	13000 at -10	60,000 at -15	9.3		
20			5.6	<9.3	2.6
30			9.3	<12.5	2.9
40			12.5	<16.3	2.9*
40			12.5	<16.3	3.7 [†]
50			16.3	<21.9	3.7
60			21.9	<26.1	3.7

*—0W-40, 5W-40, 10W-40 grades.

[†]—15W-40, 20W-40, 25W-40, 40 grades.

Source: SAE J300, Dec. 1999.

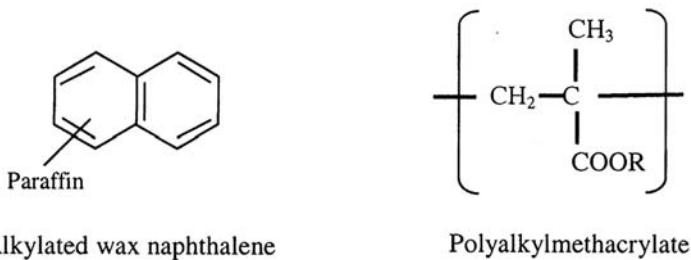


Figure 35 Examples of pour point depressants.

viscosity for passenger car motor oils in Europe is moving into line with North America, where most of the gasoline oils are 5W-30s with HTHS limits in line with the SAE J300 specification. In addition, some OEMs are now using 5W-20 oils for factory fill to ensure even better fuel economy. This is important since some viscosity modifiers have poor temporary viscosity-loss performance at high temperatures. If an HTHS of greater than 3.5 cP is required, then it is easiest to formulate this oil with an OCP. If the HTHS target is less than 3.5 cP, most viscosity modifiers will suffice.

6.6 Viscosity Modifier Requirements

The necessary attributes for polymeric viscosity index improvers are as follows:

- Good thickening for cost-effectiveness
- Proper shear stability to stay in grade
- Temporary shear stability to meet high-temperature, high-shear requirements (especially where it is specified)
- Minimum low-temperature viscosity for cold cranking and pumping
- Minimal deposits at high temperature, e.g., pistons and turbochargers

Correct selection of the VM will allow all the viscometric requirements to be achieved at the optimum cost. Once this is done, it is then necessary to evaluate the formulation in the various engine and field tests. The performance of the VM in the engine and the service duty requirements will then define if the VM is suitable for the intended application.

7 POUR POINT DEPRESSANTS

All mineral base oils contain some paraffinic components. These have very good viscosity-temperature dependence, but they are liable to form waxes at lower temperatures. While the effective volume of these waxes is low, they can still form a network of wax crystals that prevents the oil from flowing. One way to investigate this phenomenon is to measure an oil's ability to flow at low temperatures by way of its pour point. The pour point temperature of an oil is defined as the lowest temperature at which the oil is still capable of flowing and is measured according to ASTM D97. Additives used to reduce the pour point temperature may also benefit the low-temperature pumping viscosity.

Pour point depressants work at low temperatures, not by preventing wax crystals from forming, but by minimizing the formation of wax networks and thereby reducing the amount of oil bound up in the network. Examples of pour point depressants include polyalkylmethacrylates, styrene ester polymers, alkylated naphthalenes, ethylene vinyl acetate copolymers, and polyfumarates. Treat rates are typically less than 0.5%.

8 FOAM INHIBITORS/ANTIFOAMS

Entrained gas or foaming of a lubricant will reduce its effectiveness and needs to be minimized and at best stopped from building up during engine operation. In engine oils the presence of foams can result in reduced oil pressure, leading to engine damage particularly for hydraulic lash adjusters or for hydraulically actuated unit injectors. Air entrainment is another problem. This may lead to cavitation of the oil film in bearings and possible failure. The performance of hydraulically actuated unit injectors is also sensitive to the amount of entrained air.

For simple oil formulations a foam inhibitor may not be necessary. However, the stability of foams increases as more additives are added to the lubricant. This has necessitated the use of foam inhibitors such as

- Dimethylsiloxane polymers
- Alkylmethacrylate copolymers
- Alkylacrylate copolymers

These compounds have borderline solubility in the lubricant and function by reducing the surface tension at the interface of the air bubble, thus allowing the bubble to burst more easily. To function effectively they must be present as a fine dispersion.

Foam inhibitors are usually added to the lubricant at very low levels, typically less than 20 ppm. At higher levels the solubility becomes an issue and is noticeable by an increase in the cloudiness of the lubricant and possible dropout of the foam inhibitor.

Foaming is measured according to ASTM D892, which uses air flowing through a porous ball to create foam in the test oil sample. The amount of foam and its stability are measured at 24°C and 94°C. ASTM D6082A is a variation of this test but measures foaming at 150°C. Additional engine tests such as the Navistar HEUI have also been introduced for diesel oils since API CG-4. This test measures a diesel oil's ability to minimize air entrainment that could affect the performance of the unit injectors, which are hydraulically actuated. Gamma-ray detection techniques are also being used to monitor the entrained air in an engine by way of the oil density. BMW uses this method for its oil approvals system.

REFERENCES

1. D Klamann. Lubricants and Related Products. Hamburg: Verlag Chemie, 1984.
2. RM Moitier, ST Orszulik, eds. Chemistry and Technology of Lubricants. London. Blackie Academic & Professional, 1997.
3. CV Smalheer, RK Smith. Lubricant Additives. Cleveland, OH: The Lezius-Hiles Co., 1967.
4. WC Gergel. Detergents: What are they?" presented at the JSLE/ASLE Meeting, Tokyo, Japan, June 10, 1975 (and references therein).

5. KL Kreuz. Gasoline engine chemistry as applied to lubricant problems. *Lubrication* 55:53–64, 1969.
6. KL Kreuz. Diesel engine chemistry as applied to lubricant problems. *Lubrication* 56: 77–88, 1970.
7. S Roby et al. *Lub Eng* 50(12):989–955.
8. K Inoue, H Watanabe. *ASLE Transactions* 26:189–199, 1983.
9. S Korcek et al. *SAE* 810,014.
10. R Jones, RC Coy. *ASLE Transactions* 24(1):77–90.
11. R Jones, RC Coy. *ASLE Transaction* 24(1): 91–97.
12. M Kawanura et al. *SAE* 852,076.
13. H So, YC Lin. *Wear* 177:105–115, 1994.
14. AG Papey. *Lub Sci* 10–3, May 1998.
15. JJ Habeeb, WH Stover. *ASLE Transactions* 30(4):419–426.
16. PG Harrison, P Brown, J McManus. *Wear* 156:345–349, 1992.
17. JM Georges et al. Presentation from 53rd Annual Meeting of STLE in Detroit, Michigan, May 17–21, 1998.
18. PA Willermet et al. *Tribology Int* 28:163–175, 1995.
19. C Eberan-Eberhost et al. Ash-forming extreme pressure/anti-wear lubricant additives. Paper presented at the seminar “Additives for Lubricants” held at TAE, Esslingen, Germany, December 11–13, 1991.
20. PA Asseff. U.S. Patent 2,261,047 (4/28/45, assigned to Lubrizol).
21. U Ingold. Inhibition of Autoxidation of Organic Substances in Liquid Phase 61: 563–589, 1966.
22. D Johnson, S Korcek, M Zinbo. Inhibition of oxidation by ZDTP and ashless antioxidants in the presence of hydroperoxides at 160°C. *Fuels and Lubricants Meeting*, San Francisco, Oct. 31–Nov. 3, 1983, pp 71–81.
23. M Rasberger. Oxidative degradation and stabilization of mineral oil-based lubricants. In RM Mortier, ST Orszulik, eds. *New York: Publishers*, 1992, pp 83–123.
24. HH Abou El Naga, AEM Salem. Effect of worm metals on the oxidation of lubricating oils. 96:267–283, 1984.
25. KU Ingold. *J Phys Chem* 64:1636, 1960.
26. S Al-Malaika, A Marvgy, G Scott. 33:1455–71, 1987.
27. C Hamblin, U Kristen, D Chasan. A Review: Ashless antioxidants, copper deactivators, and corrosion inhibitors, their use in lubricating oils, 2:287–318, 1990.
28. G Scott. New developments in the mechanistic understanding of antioxidant behavior 35:123–149, 1979.
29. B Bhushan, BK Gupta. *Physics of Tribological Materials*. New York: McGraw Hill, 1991, Chapter 3; DH Buckley, *Properties of Surfaces*, vol. II, Theory and Design. Boca Raton, FL: CRC Press, 1983, pp 17–30.
30. R Lansdown. Extreme pressure and anti-wear additives. Ed In RM Mortier, Orszulik. *New York: VCH Publishers*, 1992, pp. 269–281.
31. J Crawford, A Psaila. Miscellaneous additives, In RM Mortier, ST Orszulik. *New York: VCH Publishers*, 1992, pp 160–173.
32. HC Freuler. U.S. Patent 2,364,283 (12/5/44, assigned to Union Oil Co.).
33. W Schreiber. U.S. Patent 2,370,080 (2/20/45, assigned to Atlantic Refining Co.).
34. Lubrizol’s internal documentation, 1992.

Additives for Industrial Lubricant Applications

JOSEPH M. PEREZ

The Pennsylvania State University, University Park, Pennsylvania, U.S.A.

1 INTRODUCTION

This chapter focuses on additives and additive chemistry. It reviews some of the history of additives, the types of additives used to improved performance in industrial applications, and the health and safety issues involved. The discussion is limited to additives used in liquid lubricants. The complexity of the chemistry and the large number of additives make it imperative at times to narrow our focus, and the liberal use of references avoids repeating information adequately described elsewhere.

As defined in this chapter, an *additive* is something added to a substance to improve its properties or performance. Additives are used widely in many applications in many industries. Some of the largest users of additives are the food, soap and detergent, pharmaceutical, petroleum, and automotive industries. These industries use additives in almost every product. Materials processing such as metal-forming and metal-working lubricants use many additives to improve performance of the lubricant and the safety and health of the user. The automotive industry and their suppliers use additives in many manufacturing processes including metal processing, corrosion protection applications, painting, glass, fabrics, plastics, and others. The petroleum industry supplies fuels and lubricants whose performance is enhanced by the use of additives, and on and on.

Searching for additive information on the Internet results in hundreds of thousands of hits ranging from applications, products, suppliers, to technical information. By adding specific restrictions to the search, these can usually be reduced to one thousand to three thousand in number. This demonstrates the broad scope of the additive industry.

2 HISTORY OF ADDITIVES

A history of the use of additives goes back even before the alchemists attempted to change lead into gold some 2000 years ago. Some of the earliest chemists to use additives were the perfume makers, hundreds of years before Christ. Perfume making was one of the earliest industries. The chemists were primarily women who produced products to make the bathing and the odiferous nature of the times more acceptable. Some 2000 to 3000 B.C., Egyptian societies used bitumen and additives for embalming and mummification. Around 1500 B.C. the Egyptians may have also used water-based additives to deliver the huge stones to the building sites of the early Pyramids. Most certainly, there were earlier applications involving the lubrication of wheels and axles with mixtures of animal fats and natural oils. The earliest reported evidence of solid film lubrication were metal inserts in wooden implements found in the Middle Ages, around 500 A.D. [1].

More recently, the science and use of additives stem from the demand for improvements in performance resulting from the development and increased use of machinery as a result of the industrial revolution, 1700–1800. Addition of inorganic chemicals to water and the use of animal fats, vegetable oils, and fish oils were common. Little obtained a British patent issued in 1849 [2] that proposed mixing fatty acid soaps with petroleum oils to produce greases.

The use of petroleum and petroleum additives in the United States quickly followed the discovery of oil in Titusville, Pennsylvania, in August 1859 [3]. In the first three decades of the 20th century, the industries leading the development and use of additives were power plants, industrial cutting fluids, railways, and the internal combustion engine [4]. The early additives in these industries were animal fats, fish oils, vegetable oils, and blown rapeseed oils that were mixed with petroleum fractions to reduce friction. Rosin oil, mica, and wool yarn were among the early grease additives. “Flowers of sulfur” was added to mineral lard cutting oils in 1916 to improve the machining of metal. About the same time, the use of phosphorus additives made their appearance as antiwear and friction improvers.

Many advances and refinements in petroleum processing in the early 1900s resulted in continuous improvements in the quality of the petroleum fractions produced such as distillates used as base stocks for lubricants. However, the improvements in the performance of industrial lubricants since the late 1930s, for the most part, have resulted from the use of additives. By the 1950s over 3000 additive patents were issued. The rapid growth of the additive market in the 1900s is found on [Figure 1](#).

A chronology of the development of some additives is found in [Table 1](#). Several additive reviews of historic value include those found in [5–9].

3 DESIRED ADDITIVE PROPERTIES

Each industry as we know it today has its own history and additive culture. For the most part, the types of additives used in different industries can differ significantly. For example, additives used in food processing have different performance and health and safety requirements than they do when used in fuels and lubricants in the automotive industry. On the other hand, there are many chemical compounds used as additives in different industries with the same or similar chemical structures.

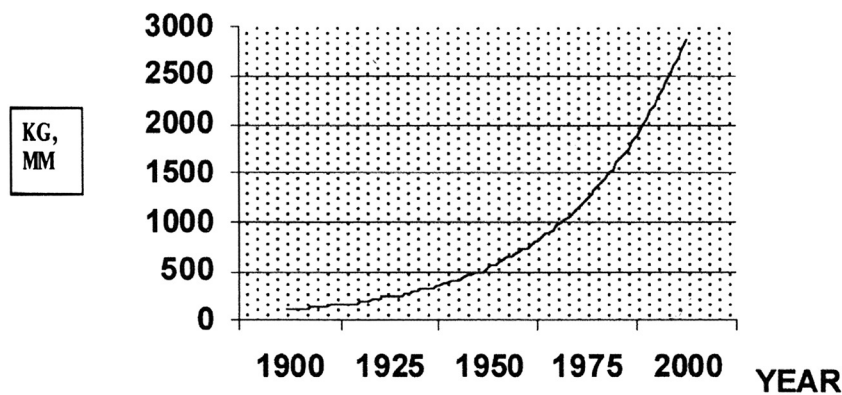


Figure 1 Trend of additive growth.

Often they perform the same function. A good example is alpha tocopherol, Vitamin E. It is used as an antioxidant in food products and in petroleum products, where it is used to maintain the stability of high-quality white oils that are used as base oils in automotive lubricants.

Although most industries have specific performance requirements related to their use of additives, some general requirements of additives apply to all applications. These include

Table 1 History of Additive Development

Period	Application	Additive	Comments
B.C.	Wheels	Animal fats, oils	Chariots, carts
B.C.	Construction	Water	Pyramids
1500	Wire drawing	Wax	Au, Ag metals
1750	Machinery	Water	Industrial revolution, cooling
1800	Machinery, metal working	Water plus inorganics	Rust prevention
1900	Industrial	Phosphorus, sulfur	Oxidation, wear, greases
1920	Metal working	Emulsifiers	Soluble oils
	Automobiles, engines	Fatty acids	Friction reduction
1930-	Engine oils	Isoparaffins, polymethacrylates	Pour point depressants
	Gears	Lead soaps	EP wear protection
1940	Engines	Calcium carboxylates	Detergents
	Engines	Zinc dithiophosphates	Antiwear/antioxidant
	Engines	Sulfonates, phosphonates, phenates	Detergents
	Oils	Synthetic base fluids	Military equipment
1950+	Metal working	Soluble oils	Cooling capability
	Engine oils	Viscosity modifiers	Temperature-viscosity improvers
		Basic sulfonates, overbasing, salicylates	Detergents, dispersants, acidity, oxidation

1. Effectiveness. The additives must be effective in performing the desirable function.
2. Solubility. The additives must be soluble in the base fluid; in some applications, this may require solubility in water. In the pharmaceutical area, vitamins are divided between fat-soluble (Vitamins A, D, E, and K) and water-soluble (B and C). In the metal-working industry there are water-soluble and oil-soluble lubricant formulations.
3. Stability. The additives should have good stability to ensure acceptable performance over time. Lack of additive stability can also affect the color and odor of the product.
4. Volatility. Volatility control is important. Low or high volatility may be required depending on the application. In some cases low volatility is required to keep the additives in solution at high temperatures. In other cases, such as vapor-phase corrosion inhibitors, the additives must have a controlled rate of volatility.
5. Compatibility. The additives must be compatible with other components in the systems. Component compatibility involves compatibility with other additives as well as with system components, such as seals, gaskets, hoses, etc.
6. Odor. Odor must be acceptable. Odor can be either desirable (perfumes) or undesirable (rancidity in lubricant reservoirs).
7. Controlled activity. The additive must have controlled activity over the lifetime of the application. The controlled activity of the additive can affect its useful life and performance in the system or product.
8. Flexibility. Lastly, there must be some flexibility on the type of additive or combination of additives used. This is important economically to allow the manufacturer to compete with competitors. Changing environmental concerns and health and safety issues may result in the need to eliminate or reduce the concentrations of additives. Optional strategies are required to make these changes and to maintain the system's effectiveness.

4 TYPES OF ADDITIVES

Some of the more common types of additives and their function are found in [Tables 2](#) and [3](#). The additives may also be characterized by how they function, i.e., physical interaction or chemical interaction. Those listed as functioning by physical interaction, [Table 2](#), act through physical adsorption–desorption phenomena (water repellants, pour point depressants, oiliness compounds, color stabilizers), changes in structural form with changes in temperature (VI improvers), changes in surface or interfacial tension (antifoam, emulsifiers), formation of structures that trap base fluid (tackifiers, thickeners, fillers), evaporation, partial pressure, or structure bond changes (odorants, color stabilizers).

Those interacting chemically react with the surfaces or other chemical species in the fluid system and, in time, are “used up” in the process. A chemical process can also increase the physical process. Oxidation results in increases in volatility when the antioxidants do not effectively control the oxidation. The oxidation of the base fluid results in degradation, producing smaller molecules that are more volatile than the original molecules.

Table 2 Additives That Function by Physical Interaction

Additive	Function
Water repellent	Impart water resistance to greases and other lubricants
Pour point depressant	Lowers low-temperature fluidity by slowing formation of waxy crystals
Visc. index improver	Improve viscosity-temperature characteristics
Antifoam	Prevents the formation of stable foam
Tackiness	Improve cohesion of fluid, nondrip quality
Emulsifier	Reduces interfacial tension, allows dispersion of water
Thickener, solid filler	Converts oil into solid or semisolid lubricant
Color stabilizer	Slows darkening of fluids
Oiliness	Improve sliding of surfaces
Odor control	Prevent or mask undesirable odors, or maintain odor level

Some additives involve both physical and chemical processes. Oiliness additives, depending on their structure, can adsorb on the surface to form films that reduce the friction between the moving surfaces. A polar head adsorbs onto the surface with the long slippery hydrocarbon chain exposed to the moving surfaces, reducing the friction. They can also contain polar elements that adsorb and chemically react with the surface to form a protective film.

Viscosity-temperature additives are very high-molecular-weight compounds that function by physically changing form with changes in temperature. However, they can be depleted chemically through thermal or oxidative breaking of bonds, or they can be mechanically sheared to form smaller, less effective molecules. The stability of the VI improvers depends on both the chemical structure and the size of the molecule. Antioxidants can chemically interact with free radicals and with

Table 3 Additives That Function by Chemical Interaction

Additive	Function
Antioxidant	Slow oxidation and oil deterioration; increase oil and machine life
Anticorrosion	Protect surfaces against chemical attack
Antiwear	Reduce thin-film, boundary wear
Detergent	Keep surfaces clean
Dispersant	Suspend and disperse undesirable combustion, wear, and oxidation products
Basicity control	Neutralize acids from oxidation processes
Antirust	Eliminate rust due to water or moisture
Oiliness	Reduce friction, increase lubricity
Extreme pressure (temperature)	Prevents seizing, increases load-carrying ability
Metal deactivator	Counteracts catalytic effects of surfaces by passivating surfaces
Antibacteria	Prevent or slow growth of bacteria in systems
Antiseptic	Prevent emulsion breakdown or odor from growth of bacteria

hydroperoxides to slow the chain reaction that results in oxidation of the base fluid. Some additive molecules such as phenothiazines used in ester formulations can react many times with oxygen molecules before they are depleted.

Antiwear and EP-type additives both react with the surfaces to form a chemical film that is sheared more easily than the moving metal surfaces. Whether it is antiwear or EP depends on the load the film formed can carry and how it handles the high temperatures generated by the friction forces. Although bulk oil temperatures may be low, the temperatures at the metal-to-metal interfaces in the contact zone can exceed 300°C. At extreme loads the frictional heat can exceed the melting temperature of the metal.

In some cases the films formed need to be continuously resupplied to function properly (some chlorine- and sulfur-containing films), while others (some phosphorus films) form a thick film that endures for extensive periods of time after the additive in the formulation is depleted. In other cases the effectiveness may depend on the structure of the base fluid.

Some additives, e.g., zinc dithiophosphates, alkyl amines, are dual functional additives. They can function as antioxidants and antiwear additives, or as antiwear and surface deactivators. The zinc dithiophosphates (ZDDP) are some of the most economical and effective additives. Although their largest application is in the formulation of automotive and diesel engine oils, they are used in industrial hydraulic fluids. Depending on the mix of hydrocarbon moiety, i.e., primary alkyl, secondary alkyl, or aryl, the temperature at which the additive is most effective can be controlled. The use of this type of additive in oils is an example of the complexity of the additive industry. Even though the additive is effective and economical, it has come under scrutiny from an environmental viewpoint in automotive engine oils. The phosphorus and sulfur in the additive are suspected of being detrimental to the effectiveness of aftertreatment catalysts in spark and compression ignition engines. In engine oils a serious problem exists in trying to come up with a solution. Alternative additives, evaluated to date, are not as effective and are significantly more expensive than the ZDDPs. Since combustion is not a factor in industrial applications, there is no problem with using this type of additive.

Each additive has its own mechanism(s) as to how it works physically or chemically. These mechanisms are well described in the literature, and no attempt will be made to definitively describe these mechanisms for the additives found in [Tables 2](#) and [3](#). However, some of the additive chemistry of the more common additives are briefly reviewed and the reader is referred to relevant, comprehensive literature on the mechanisms.

5 ADDITIVE CHEMISTRY

The understanding of chemical mechanisms involving industrial lubricants and the role of additives blossomed in the 1940s and 1950s partly as a result of the demands of the military during World War II. The need for better aviation lubricants, vehicle fuels, weapons lubricants, and corrosion and wear protection was due to the environments involved in the war. These environments ranged from extreme low temperatures in the Aleutian Islands, North Atlantic, and Russia to the hot, dry Sahara Desert in Africa and the hot and humid South Pacific. Following the war,

the rapid advances in engine and industrial technology continued to influence the development of new additive technology. Higher operational speeds in engines, more power per unit weight, increased metal surface temperatures, more complex hydraulic systems, higher pressures, and higher lubricant temperatures required better thermal and oxidation stability, improved friction and wear characteristics, and rheological properties for the lubricants of the day. The introduction of the turbojet engines and subsequent jet engines led to unprecedented advances in engine and lubricant additive technology. Manufacturing processes and industrial machining technology had to advance also. Robotics and improved hydraulic systems were developed to meet the challenges.

Research on oxidation mechanisms and oxidation inhibitor additives during this time period were led by Booser [10–12], Dennison [13], Larson [4], Stewart [8], Zuidema [14], and others. Outstanding research laboratories of major oil companies and additive suppliers, government laboratories such as NBS (now NIST) and Argonne National Laboratory and University laboratories, such as the Petroleum Refining Laboratory at the Pennsylvania State University, Draper Laboratory at the Massachusetts Institute of Technology, Armour Labs at the Illinois Institute of Technology, and others, many of which no longer exist, were deeply involved in independent and collaborative research of the era.

The primary function of an antioxidant is to reduce oxidation by interaction with free radicals or decomposition of hydroperoxide species that promote oxidation. Compounds containing amine and phenol groups are effective against free radicals. Compounds containing sulfur and combinations of phosphorus and sulfur are effective against hydroperoxides [15,16]. Some metal-containing compounds such as copper naphthenates can be pro-oxidants or effective antioxidants depending on the system and the additive concentration [17–19].

Metal deactivators also reduce the effect of metals and their salts on the rate of oxidation of the bulk fluid [20]. Some of these compounds such as ethylenediaminetetraacetic acid (EDTA) complex with the metal particles suspended in the fluid, rendering them inactive.

To be effective, antiwear (AW) additives form protective films by chemical or physical reaction with the surface [21–25]. They minimize the removal of metal through formation of lower shear-strength films that reduce friction, decreasing the contact temperatures or by increasing the contact surface reducing the effective load. The most effective additives contain sulfur or phosphorus, or both, that reacts with ferrous metals. Hundreds of technical papers have been written on the performance and mechanisms of TCP and ZDDP [26–31]. Extreme-pressure (EP), or more correctly extreme-temperature, additives also contain phosphorus or sulfur compounds, but chlorinated compounds are also effective [32]. The use of phosphorus compounds started around the time of World War I, and the addition of sulfur and chlorine to gear oils began in the 1930s [33]. Most of the more effective EP gear oils in the 1960s and 1970s contained combinations of sulfur, phosphorus, and chlorine. The use of chlorine-containing AW and EP compounds is gradually declining due to environmental concerns, with some suppliers developing new replacement products [34].

In nonferrous systems, such as ceramics, copper, or aluminum alloys, the mechanism stays the same but the interaction with the surfaces changes. Alcohols, esters, vegetable oils, and long-chain hydrocarbons can be more effective than the

sulfur and phosphorous compounds used as antiwear and EP additives in ferrous systems [35,36].

Corrosion and rust inhibitors absorb on the surface, forming a barrier hydrocarbon film against water and corrosion-causing materials. These are often basic amine-type compounds that have the ability to neutralize acids. They may also passivate the metal surface, reducing the catalytic or accelerating effect on oxidation of the oil [37,38].

Dispersants slow the formation of deposits and sludge by dispersing the precursors and insoluble particles in the fluid. These, like detergents, are large molecules with polar and nonpolar segments. Detergents also contain moieties that can neutralize acids produced by oxidation of the oil or, in IC engines, combustion. The combustion products get into the fluid as a result of blow-by. Typical dispersants are succinimides, succinates, and Mannich-type reaction products. Detergents can be phenates, sulfonates, and salicylates [21,39]. Normally, dispersants and detergents are not required in industrial gear oils, turbine oils, or industrial hydraulic fluids. Still, dispersants and detergents are the largest selling additives (see Figure 2).

Foam inhibitors prevent formation of foam by changing the surface tension, which results in the collapse of gas bubbles as they form [40,41]. The inhibitors are high-molecular-weight polymers that are relatively insoluble in the oils. The defoamers are often blended into a more soluble solvent system and added in parts per million. Air entrainment is often mistaken for foaming in hydraulic systems. Additives can sometimes help with air entrainment, but usually changes to the system to prevent air entering the system or modifying the base fluid is a better approach. Polydimethylsiloxanes, polydiarylsiloxanes, mixed siloxanes, and polyglycol ethers are examples of these additives. Friction modifiers are added to lower the energy requirements of a system by reducing the friction of the system. These additives are often long-chain hydrocarbon molecules with one end of the molecule containing a polar group that is adsorbed on the surface [42–44]. Oleic acid and other organic fatty acids, alcohols, and amides are typical of this type of friction modifier. Graphite or molybdenum compounds suspended in the fluid may also act as modifiers. More recently, nanoparticles of these solids and teflons are of high interest in this area. Some friction modifiers, such as alkyl phosphites and phosphate esters, can also function as antiwear compounds.

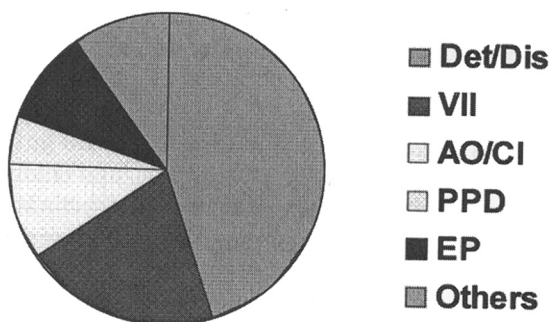


Figure 2 Additive breakdown (lubricants).

Rheological properties of industrial oils are important factors in their performance in a system [45–48]. Additives are used to modify the temperature-viscosity characteristics in some applications such as motor oils. These viscosity index improvers (VII) are usually high-molecular-weight polymers that are compact molecules at low temperatures and expand in size as the temperature increases. Acryloids, polymethacrylates, and various copolymers such as styrene-butadiene were some of the earlier VII additives.

The other major concern of the viscosity characteristics of a fluid is the viscosity at low temperatures. Paraffinic base oils become very viscous at low temperatures unless the high wax content is removed while some isoparaffinic and naphthenic base oils are fluid down to temperatures below -40°C . Synthetic fluids have a low-temperature advantage in that most synthetic fluids have excellent low-temperature properties. Natural oils are solids or have viscous pour points by about 0°C . Pour point depressant additives are often used to interfere with the crystalline network formed in these oils at low temperatures. The effectiveness depends on both the type of fluid and the chemical structure of the additive used. Some commercially available additives are effective in mineral oils but have limited or no effect in natural oils. Evaluation of concentration levels and fluid blending is required to achieve the maximum low-temperature properties for these additives. Some of the newer Type II and Type III base fluids contain high levels of isoparaffinic molecules and have acceptable pourpoints without the need of pourpoint depressants. Natural oils, on the other hand, may require blending with synthetic fluids and pour point depressants to achieve the necessary viscosity levels for multiviscosity-grade oil applications.

Other system components such as seals and gaskets can shrink, swell, crack, or otherwise deteriorate if they are not compatible with the fluids used. Aromatic fractions can sometimes be added as blending components to modify the fluid properties. However, environmental concerns over the potential carcinogenicity of aromatic fractions are resulting in less use of aromatic fractions to improve seal swell characteristics. More effort is now required to ensure fluid compatibility with the proper seal materials to prevent oil leaks. Additives, such as organic phosphates, may still be used. The better approach, especially for synthetic fluids, is to blend the base fluids to achieve the desired results. A good example would be using mixtures of synthetic hydrocarbons, such as polyalphaolefins and esters to achieve desired seal swell results.

In the case of water-based fluids such as hydraulic, metal-working, water-glycols, antifreeze and other similar fluids, the use of demulsifiers, emulsifiers, biocides, and corrosion prevention additives is often required.

Metal-working fluids can contain antiwear, EP, antimist, corrosion inhibitors, biocides, antifungicides, defoamers, couplers, and dyes. Dyes are often used to identify fluids by application. Hydraulic fluids were often dyed red and coolants green during World War II to make it easier for technicians to properly maintain equipment. The original MIL-L-Spec-5606 Red Oil was used as an aircraft hydraulic fluid in World War II in many aircraft. This oil was composed of a light Winkler, low pour naphthenic base oil containing some phenolic antioxidant, a polymethacrylate viscosity improver, and tricresyl phosphate as an antiwear additive. The oil was a very effective and stable formulation. This was dramatically proven with the finding of the “Lady Be Good” B-24 bomber in the Sahara Desert some 15 years after the war. The fluid recovered from the aircraft showed no loss of performance after some

15 years of cycling from high to low temperatures in the temperature extremes of the Libyan desert. Oxidation stability and wear properties of the fluid were unchanged.

6 RECOMMENDED LITERATURE

The reader is referred to some general references for additional details on the chemistry of these additives [49–53]. For details on synthetic fluids and the additives used in these fluids, [54] is recommended. This reference includes an extensive discussion of metal-working fluids and focuses on polyalkylene glycol synthetic (chemical solution) metal-working fluids.

Numerous publications have been referenced where appropriate throughout this chapter that supply background and additional references. In addition, a series of books should be mentioned [55–57, 59–61, 64–67]. Although they are not new, they include searches of the patent literature. The patent literature in the United States is extensive and can be an excellent source of information. These publications are briefly described. They have been very useful to the author during his career.

The first one of interest deals specifically with lubricant additives and oxidation mechanisms [55]. This was followed up with *Chemical Technology Review* no. 145, on advances in synthetic lubricants and additives for lubricants [56]. The latter book contains chapters on dispersants and detergents, viscosity index improvers, load-carrying additives, oxidation and corrosion inhibitors, metal-working lubricants, solid lubricant composition, grease compositions, specialty lubricants, and related processes. The book also contains a company, author, and U.S. Patent Number indexes.

Chemical Technology Review no. 140 (*Pollution Technology Review* no. 64) deals with the reprocessing and disposal of oils [57]. The book contains chapters on sources and characteristics, recovery processes, proprietary processes, disposal practices, disposal of recovery residues, disposal and recycling of Air Force waste oils, combustion studies of waste POLs, municipal incinerator fuel, disposal by land spreading, and research projects. As concerns over availability of petroleum continued to grow, this area became a major area of interest during the oil crisis of the early 1980s and continues to have the interest of the technical community even today. The lubricant quality, performance, and additive issues relating to recycled oils resulted in a major government-driven research program on recycled oils involving NBS (now NIST) and a number of major industrial participants [58, 59].

Chemical Technology Review no. 112, also listed as *Energy Technology Series Review* no. 30 [60], is an extensive search of fuel additives and patent literature and includes chapters on detergents and anti-icing additives, flow improvers and pour point depressants, oxidation and corrosion inhibitors, octane improvers and antiknocks combustion aids and fuel compositions, and antistats, biocides, dyes, and others.

Two other books in the series, *Chemical Technology Review* nos. 114 and 145 (*Energy Technology Reviews* 31 and 51) [61, 62] deal with the use of methanol and ethanol as fuel additives. The first discusses methanol technology, and the second looks at ethanol. Although not much additive technology appears in these two books in the series, the increased use of these fuels is of current interest. Concerns over the use of alternative fuels in the 1980s led to considerable research on additive compatibility. Several publications dealing with the selective extraction of additives

by alcohol fuels resulting in injector deposits in diesels and increased corrosion and wear were published [63,64]. This illustrates that when dealing with additives, one must consider the entire system. Selected extraction or loss of additives may occur in industrial systems if the lubricants are in contact with dissimilar fluids.

In the process of oil recovery, a considerable amount of oil remains in the strata after the initial recovery process. A considerable amount of research on secondary and tertiary research has been conducted. These processes often utilize significant quantities of additives. Although additives are not discussed in detail, *Chemical Technology Review* no. 103 (*Energy Technology Review* no. 22), *Enhanced Oil Recovery—Secondary and Tertiary Methods* edited by M. M. Schumacher (1978, ISBN 0-8155-0692-9) [65], is a good reference for the early work in the field. Studies are reported in the literature dealing with some of the additive chemistry involved [66].

Chemical Technology Review no. 132, *Corrosion Inhibitors 1979—Recent Developments*, by J. S. Robinson (ISBN 0-8155-0797-7) [67] discusses multipurpose and highly specialized corrosion inhibitors. Chapters titles include circulating water systems, oil well and refinery applications, construction materials, fuels and lubricants, inorganic treatments of metal, organic treatments of metal, and additional applications.

Antioxidants are discussed in *Chemical Technology Review* no. 127, *Antioxidants 1979—Recent Developments*, by William Ranney (ISBN 0-8155-0747-X) [68]. The book includes chapters on polyolefin resins, polyvinyl chloride resins, polyester, polycarbonate, and polyurethane plastics, elastomers, petroleum products and synthetic lubricants, food products, and other antioxidants.

Chemical Technology Review no. 120 (also, *Energy Technology Review* no. 33 and *Pollution Technology Review* no. 53) [69] deals with problems of incomplete combustion, soot deposition, and sludge formation as related to fuels, *Boiler Fuel Additives for Pollution Reduction and Energy Saving*, edited by R. C. Eliot (1978). The book deals with mechanisms of chemical control in hydrocarbon combustion, emission-reducing additives, fuel-handling additive systems, various combustion aids, and post-flame treatments in industrial boiler applications (ISBN 0-08155-0729-1).

7 ADDITIVE SUPPLIERS

In 1997 over 2.5 billion gallons of lubricants were sold in the automotive (55%) and industrial (45%) markets (see [Figure 3](#)). Competing for this market are a large number of additive suppliers. Some of these companies make or supply one or a few specialty additive types, while others have an extensive line of additives. The one major fact is that it is a continuously changing industry. [Table 4](#) contains almost 200 companies that a trade journal reported as additive sources fewer than 10 years ago [70]. A current source of additive suppliers contains again some 200 or more suppliers, but only about 25% (*italicized companies*) of those found in [Table 4](#) are on the current list [71]. Some may have been omitted or did not supply the necessary information for the publication, but for the most part the changes are due to the nature of the industry. Acquisitions, name changes, and mergers are the primary cause for the changes. Even some of the major suppliers in [Table 4](#) have merged. Currently in the United States the four major additive suppliers are Chevron Oronite Additives Division, Ethyl Additives (also includes Amoco Additives Acquisition),

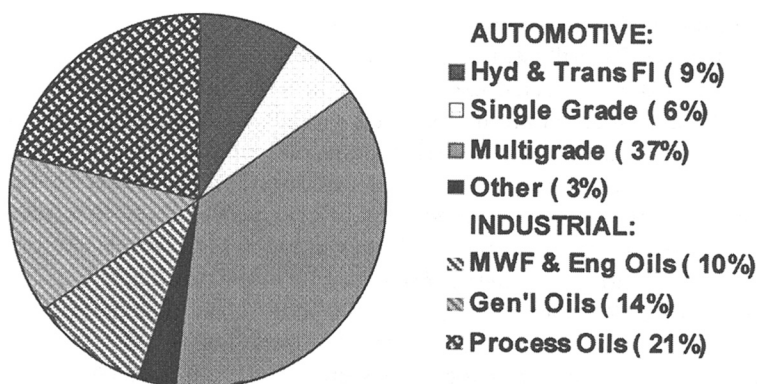


Figure 3 Lubricants 1997, 2.5 billion gallons.

Infinium (Exxon Paramins and Shell Additives merger), and Lubrizol. Many of the smaller companies continue to supply quality additives, additive packages, and formulated fluids, but the more complete series of additives can be found in the major companies. There are exceptions: Ideas, Inc. lists some 148 additives available in its product brochure. Other majors supplying industrial additives for water treatment and metal-working fluids include Nalco-Exxon, Chevron, and Witco. Overseas majors supplying additives include Ciba-Geigy, Rhein Chemie, RhoMax, Rhone-Poulenc, and Shell Additives.

8 LUBRICANT RESEARCH AND DEVELOPMENT

Often, if there is a sufficient database for a particular application, the need for a lubricant is simply a matter of contacting the appropriate suppliers and evaluating the fluids they supply in the system. However, some applications and new technology require the development of a lubricant. Developing a new lubricant for any industrial process is a difficult and time-consuming process. The process described here was used in developing a successful high-temperature liquid lubricant for advanced diesel engines [72].

The normal procedure is first to develop a tentative specification for the application and then to screen the additives and base fluids using a series of bench tests. Successful candidates are then evaluated in a full-scale system prior to selecting candidates for a field test. The actual sequence of testing depends on the application and the availability of prior data. Availability of resources, timeframe or window of opportunity, and the economics or bottom line are also factors.

Most industries maintain a database of successful and unsuccessful tests, and these are very useful in the selection of materials and tests. In addition to in-house tests and experience, most trade associations and cooperative testing organizations such as ASTM and SAE have published tests or guidelines for the evaluation of additives and base fluids.

A generalized sequence for the development of a functional fluid is found in [Figure 4](#). The first step is to establish the requirements for the desired performance

Additive Type

Additive Type																			
	1. Aftermarket additive packages 2. Antifoam 3. Antioxidants 4. Biocide 5. Corrosion inhibitor 6. Demulsifier 7. Detergent 8. Dispersant 9. Dyes 10. Emulsifier										11. Fully formulated add. packages 12. Friction modifier 13. Lubricity/EP additives 14. Metal deactivator 15. Pour point depressant 16. Pour point stabilizer 17. Tackifier 18. Thickener 19. VI improver								
Additive	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Acheson colloids												*	*/						
Akzo Chem.								*				*	*/						
Albright & Wilson Amer.					*							*	*/		*				*
Allegheny Petr. Products	*		*	*	*	*	*	*		*	*	*	*/	*	*	*	*		*
Alox Corp.					*			*				*	*/				*		
American Mftg Intl Inc.				*	*		*			*	*	*	*/						
Amsoil Inc.	*																		
Angus Chem.		*		*	*			*											
Associated Chemists Inc.	*			*	*			*					*/	-					
Ausimont USA					*														
Bardahl Mftg	*		*	*			*	*				*	*/						*
BP Oil			*		*		*	*			*				*				*
Brighton Labs			*							*	*		*/	*					
Brooks Technology					*														
Cadillac Oil			*	*	*		*	*		*		*	*/	*	*		*		*
Calgene Chem.					*					*		*	*/	-					
C. C. Custom Technology					*							*	*/	*			*		
Certified Labs/Lubemaster			*	*	*	*	*				*	*	*/	*	*	*	*		*
Chemol													*/	-					
Chemtool Inc.	*			*	*						*	*	*/	*					
Ciba Additives			*		*						*	*	*/	*	*				
Cincinnati Milicron				*	*			*					*/	*					
Climax Perform. Matls					*					*	*	*	*/	*	*				
Consultant Lubricants					*								*/	*					
Crystal Inc.		*																	
Desilube Tech			*										*/	*					
Detrex Corp.					*														
Dover Chem.			*									*	*/	*					
Dow Corning		*																	
DuPont Petrol. Additives	*	*	*		*	*	*	*			*	*	*/	*	*	*			*
Dylon Industries				*								*							
Edrich Products				*						*									
Elco Corp.			*		*	*					*	*	*/	*	*				

(Continued)

Table 4 Continued

Additive	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	1
Engineered Comp. & Lubr.													*/						
Eppert Oil										*	*								
Ethyl Petrol. Additives			*		*		*			*	*		*/	*	*		*		
Far West Oil				*	*	*		*		*	*		*/				*		
FMC Corp.													*/						
Form Cut Engrd Fluids				*	*					*			*/						
Forsyth Assoc.				*															
Functional Products					*					*	*				*		*		
Gard Corp.							*												
Gateway Add.					*					*		*	*/						
Geo. Pfau's Sons								*				*	*/						
G. Whitfield Richards										*				*					
Hammonds Fuel Additives	*			*									*/						
Henkel Corp.												*	*/				*		
Heavatex Corp.																	*		
Hoechst Celanese					*	*				*	*		-/*						
Hydrotex	*			*			*	*					*/		*				
Ideas, Inc.		*	*	*	*	*	*			*		*	*/	*	*		*		
Intl. Lubricants												*	*/						
Keil Chem. Div					*					*	*	*	*/	*					
Ferro Corp.																			
King Industries					*														
L.E. Hutchens			*			*				*	*		*/		*	*			
Lockhart Chemicals					*		*	*		*			*/						
Lowe	*											*							
Lubricant Technology										*	*		*/				*		
Lubrizol Corp.		*	*		*	*	*			*	*	*	*/	*	*	*			
Mayco Oil	*			*						*	*	*	*/						
McCollister & Co.				*		*	*			*	*		-/*		*		*		
Metalworking Lubricants	*		*							*	*		-/*				*		
Metal working				*	*									*					
Chem. & Equip.																			
Miracema Nuodex S.A.					*								*/						
Mitsui Petrochemicals Ltd.								*											
Mobil Chem.	*			*	*	*	*			*		*	*/	*					
Mona Industries				*	*	*	*			*	*	*	*/	*					
Monroe Fluid Technology				*						*			*/						
MPG Industries				*									*/						
Muscle Products	*		*	*						*	*	*	*/						
Nalco Chemical		*	*	*	*	*	*	*		*	*		*/	*	*				
Neo Synthetic Oil	*			*		*	*			*	*	*	*/			*	*		
Occidental Chemical													-/*						
Oils Unlimited																	*		
Olin Corp.				*															
Orelube	*									*		*	*/						
Oronite	*	*		*		*	*	*		*	*	*	*/						
Paramins (Exxon)		*	*	*	*	*	*	*		*	*	*	*/	*	*	*	*		
Patriot Technologies	*			*									*/						

Table 4 Continued

Additive	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Petron Intl.	*		*		*		*	*			*	*	*/	*		*	*	*	*
PMC Specialties			*	*	*									*			*		
Powell Duffryn	*						*				*		*/						
Power Up Lubricants	*										*	*							
Power-X Lubricants	*											*	—/	*					
Precision Lubricants																	*		*
Primrose Oil	*			*	*		*	*			*	*	*/	*	*				*
Protec International	*		*	*	*	*	*	*		*	*	*	*/	*	*	*	*		*
QMI-Jax												*							
Red Line Synth. Oil	*																		
Rhein Chemie			*		*	*					*	*	*/	*					
Rheox Inc.					*													*	
Rhone-Poulenc			*		*	*	*	*					—/	*					
Rohm Tech Inc.															*	*			*
Rohm & Haas				*											*				*
Rosemead Oil Products				*															*
Royal Lubr.					*														
Royal Mftg																			*
RT Vanderbilt			*	*	*							*	*/	*			*		
Shell Chemical																			*
Slick 50	*										*	*	*/	*					
Soltex																	*		
Specialty Chem Cons.	*				*		*	*			*	*	*/	*					
Stuart-Ironside	*		*								*	*	*/	*					
Super Dri Corp.	*		*		*		*						*/		*	*			
Surpass Chemicals Ltd				*	*	*			*				—/	*					
Synlube	*												—/	*					
Texaco Additives	*	*		*		*	*			*		*	*/	*	*				*
Texas Refinery	*															*			
The B.F. Goodrich																			*
Tri-State Industrial Lubr				*					*	*		—/	*				*		
Ultra Additives		*																	
Unichema NA											*								
Union Carbide Chemicals & Plastics				*															
Uniroyal Chemical				*		*													*
United Color Manufacturing									*										
U.S. Professional Lab				*															
Universal Oil	*	*				*	*			*	*	*/	*	*		*	*		*
Valvoline, Inc.				*	*	*									*				
Werner G. Smith				*	*				*			*/	—						
Witco Corp.				*	*	*			*		*	*/	*	*					
Wolfe Chemicals		*		*						*		—/	*	*	*		*		*
Wynn Oil	*		*							*	*	*/	*				*		
Biotech Intl.	*										*								
Chevron											*								

(Continued)

Table 4 Continued

Additive	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Dixon-Ticonderoga													*/*						
Mohawk Labs	*			*									*/-			*			
Poly Enviro Lab															*				
Kelco Div/Merck																		*	
Bodie-Hoover Petroleum																			*
Petroleum Packers																			*

Source: Ref. 70.

of the system. Development of a tentative specification may be based on experience with similar systems or may be a best estimate of what is going to be required for the system to operate satisfactorily. This estimate is based on the environment in which the system is to operate, the desired life of the system, and the economics. Environmental health, safety, and disposal issues have become important factors in recent years and should be considered early in the development. Once the specification is determined, the test design used in the development of the fluid depends on many factors. Often, cost rather than optimal performance is the bottom line.

Base Fluids

Once a specification or tentative specification exists, the selection of a base fluid is the next step. The selected base fluids or combination of fluids must meet the desired physical properties. The additive susceptibility can also vary with the type of base fluid used. The most effective additive–base fluid combination that meets the desired specification at the lowest cost is the development target.

The development of highly refined mineral oils or superrefined mineral oils was available in the early 1960s. These superrefined oils would meet current Type II and Type III base oil specifications. The advantage of the fluids produced in the 1960s was their improved additives susceptibility, making them competitive with synthetic fluids [73]. The cost of the fluids based on the refining technology limited the use of these fluids to the military applications for which they were designed. The same can be said for synthetic base fluids at the time. Changes in crude source quality, improvements in refining technology, and environmental factors have resulted in the current low-aromatic, low-sulfur base stocks. Current trends indicate the use of conventionally refined base fluids is diminishing. The new base stocks may require less additive to be effective, but additional problems of additive solubility, system component compatibility, and fewer additives to choose from are tradeoffs that have to be considered.

Environmental concerns are increasing the interest in synthetic fluids and natural renewable lubricant base oils including vegetable oils. Some of the natural oils have limiting physical and chemical properties, but, based on the application, these can be viable base fluids for specific applications. As with most of the newer base stock fluids, the selection of the proper additive package becomes more difficult.

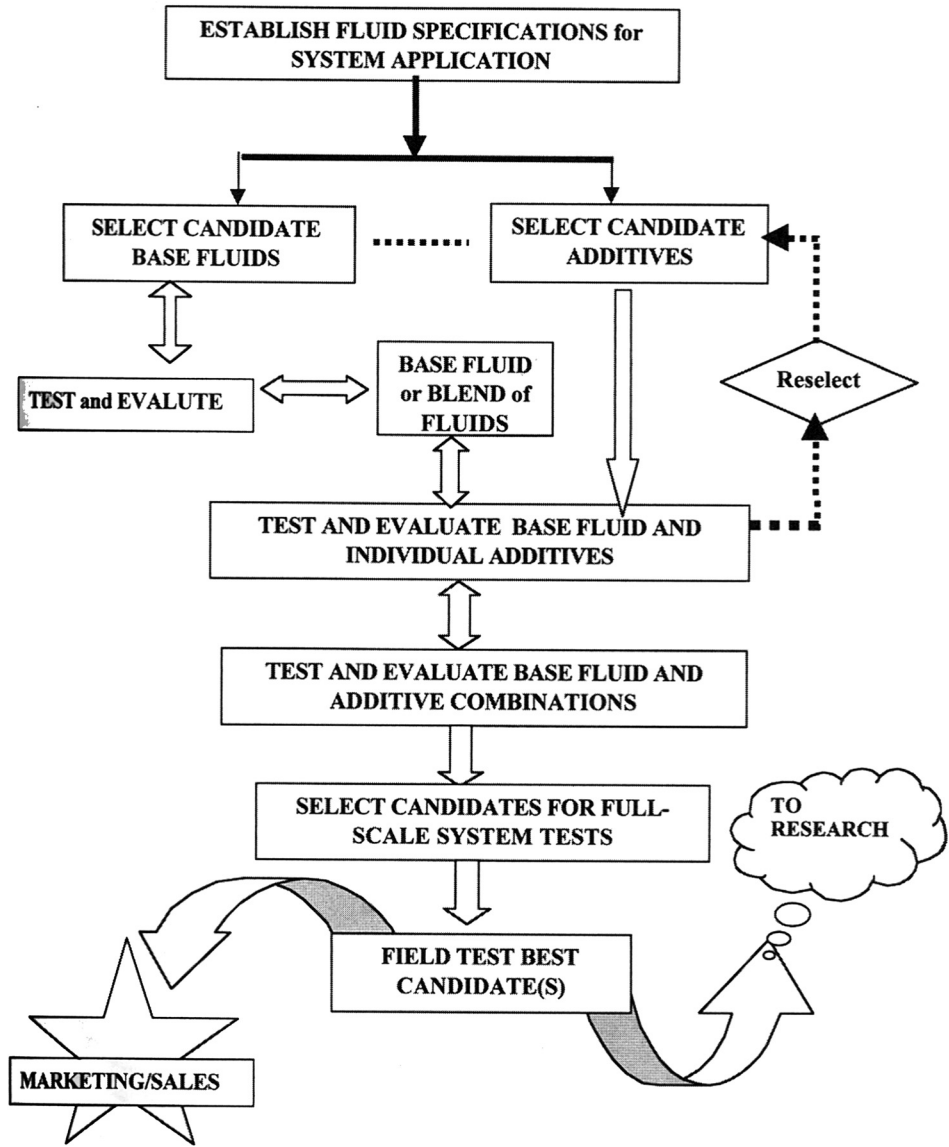


Figure 4 A sequence for the development of a functional fluid.

Additives

The list of additives available from the approximately 200 current additive suppliers is extensive. Even some of the smaller suppliers have 100 to 150 additives available. The initial list of additives selected can be narrowed depending on the application, specifications, and prior database of knowledge. Bench tests can be used to screen large numbers of additives in a relatively short period of time. The TGA and PDSC can be used to evaluate volatility, oxidation stability, and deposit-forming tendencies

[74–86]. Other oxidation tests such as the Rotating Bomb Oxidation Test (ASTM Method D 2272) and Oxidation Characteristics of Inhibited Mineral Oils (ASTM Method D 943) are examples of standard bulk-oxidation tests [87]. The PSUMOT, TFOUT, and TEOST are thin-film tests [88–90] used to evaluate thermal and oxidative stability of base fluids and additives. A review of bulk oxidation and thin-film oxidation tests is found in [73]. Most companies have a favored list of tests used for development, some of which were internally developed.

Evaluation of friction and wear can be performed on a variety of testers. ASLE (now STLE) in 1976 [91] compiled a list of 234 wear test methods. ASTM lists several friction and wear methods including four four-ball methods, ASTM Methods D 2266, D 2783, D 4172, and D 5183 [87]. Variations of the use of the four-ball test as a research tool are reported in the literature [92,93]. The Cameron–Plint and pin-on-disc tests are also widely used for evaluation of materials, friction, and wear [94,95].

The screening of additives in the base fluid is the first step of additive selection. The compatibility of additives with the fluid and whether they are compatible, synergistic, or antagonistic in the combinations must also be determined by repeating a number of the tests. The system components must also be considered in these tests. An example of a series of tests conducted in a PDSC as part of a screening test is found in Figure 5.

The proper combinations of additives may result in tradeoffs regarding oxidative stability. Tests should also be conducted on inert and proactive surfaces.

Often when two or more antioxidants are used in combination, a synergistic effect can be obtained. To optimize the effect, it is often necessary to run various combinations of the additives at different concentrations. When combining any combination of additives, one must determine the optimum concentration [96].

Basically, the development of a lubricant for any system is a complicated and expensive procedure. The norm in the lubricant business is to have an evolution of new lubricants rather than the development of completely new formulations using new chemistry.

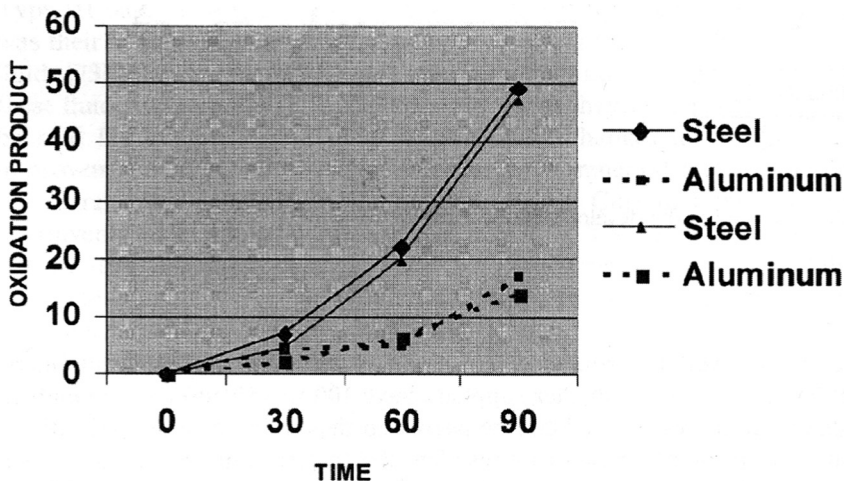


Figure 5 Effect of metal surface.

Selection of Candidates

Following a thorough screening of additives, it is necessary to evaluate the leading candidates in a full-scale test prior to expensive field testing. In some cases, such as automotive lubricants, extensive laboratory engine testing is usually conducted prior to conducting certification tests for a new engine lubricant where a series of tests is specified by consensus of ASTM engine committees [97]. The same is true in industrial applications where tests are designed to meet the requirements of the system. Full-scale hydraulic pump stand tests, gear tests, hydraulic hose testing, aluminum rolling tests, etc. are examples of systems that utilize tests designed using the major component of the system.

Field Tests

Finally, if a candidate is successful, a field test is normally conducted. The extent and type of the testing depend to some degree on the application. The common factor in field testing is that tests are expensive to conduct properly but should be used to verify additive effects in the real world [98].

The next step if the field test is successful is to turn the product over to marketing and sales. Marketing, sales, and manufacturing should all be involved in the process from the beginning to ensure no show stoppers occur upon completion of the research and development process.

REFERENCES

1. D Dowson. History of Tribology. London: Longman Group Ltd., 1979.
2. British Patent 12,571; April 16, 1849.
3. PA Dickey. The first oil well. *J of Petr Tech*, pp 12–26, Jan. 1959.
4. CM Larson, R Larson. Lubricant additives. In O'Connor and Boyd, eds. *Standard and Book of Lubrication Engineering*. New York: McGraw Hill, 1968.
5. CV Smalheer, A Mastin. Lubricant additives and their action. *J Petr Inst* 42(395): 337–346, 1956.
6. HH Zuidema. *The Performance of Lubricating Oils*, 2nd ed. New York: Rheinhold, 1959.
7. WA Zisman, CM Murphy. *Advances in Petroleum Chemistry and Refining*. New York: Interscience, 1960.
8. WT Stewart, FA Stuart. In J McKette Jr, ed. *Advances in Petroleum Chemistry and Refining*, Vol 7, Ch 1. New York: John Wiley and Sons, 1963.
9. CV Smalheer, S Kennedy. *Lubricant Additives*, SN Bowen, RG Harrison, eds. Cleveland: The Lubrizol Corp., The Lezius-Hiles Co., 1967.
10. ER Booser. PhD thesis, The Pennsylvania State University, 1948.
11. ER Booser, GS Hammond. *J Amer Chem Soc* 76:3861, 1954.
12. ER Booser et al. *J Amer Chem Soc* 77:3233 and 3380, 1955.
13. GH Dennison, Jr., PC Condit. *Ind & Eng Chem* 37:1102, 1945.
14. HH Zuidema. *Chem Rev* 38:197, 1946.
15. MD Johnson, S Korcek, M Zimbo. Inhibition of oxidation by ZDTP and ashless antioxidants in the presence of hydroperoxides at 160°C, SAE SP-558, *Lubricant and Additive Effects on Engine Wear*, 1983. pp 71–81.
16. G Scott. Synergistic effects of peroxide decomposing and chain-breaking antioxidants. *Chem and Ind* p 271, 1963.
17. DB Clark, EE Klaus, SM Hsu. The role of iron and copper in the oxidative degradation of lubricating oils. *Lubr Engr* 41(5):280–287, 1985.

18. RM Mortier, ST Orszulik. *Chemistry and Technology of Lubricants*. Suffolk, Great Britain: Blackie Academic and Professional, 1997.
19. JHT Brooke. Iron and copper as catalysts in the oxidation of hydrocarbon lubricating oils. *Disc of the Faraday Soc* 10:298–307, 1951.
20. U.S. Patent 7,776,524 (1993, Klaus et al.).
21. SQA Rizvi. Additives—chemistry and testing. In ER Booser, ed. *STLE Tribology Data Handbook*, Boca Raton, FL: CRC Press, 1997.
22. SH Roby, ES Yamaguchi, PR Ryason. Lubricant additives for mineral based hydraulic oils. In GE Totten, ed. *Handbook of Hydraulic Fluid Technology*, Ch 15. New York: Marcel Dekker, 2000.
23. TV Liston. Lubricating additives—what they are and how do they function. *Lubr Eng* 48(5):389–397, 1992.
24. HA Spikes. Additive-additive and additive-surface interactions in lubricants. *Lubr Sci* 2-1:4–23, 1988.
25. DB Barton et al. Preferential adsorption in the lubrication process of zinc dialkyldithiophosphate. *ASLE Trans* 16(3):161–167, 1972.
26. JM Perez et al. Characterization of tricresylphosphate lubricating films using micro-Fourier transform infrared spectroscopy. *Trib Trans* 33(1): 131–139, 1990.
27. S Jahanmir. Wear reduction and surface layer formation by a ZDDP additive. *J Trib* 109:577–586, 1987.
28. FG Rounds. Some factors affecting the decomposition of three commercial zinc organic phosphates. *ASLE Trans* 18:78–89, 1976.
29. H Spedding, RC Watkins. The antiwear mechanism of ZDDPs, Part I. *Trib Intl* 15:9–12, 1982.
30. RC Watkins. The antiwear mechanism of ZDDPs, Part II. *Trib Intl* 15:13–15, 1982.
31. RC Coy, RB Jones. The thermal degradation and E.P. performance of zinc dialkyldithiophosphate additives in white oil. *ASLE Trans* 24:77–90, 1981.
32. L Taylor, A Dratva, HA Spikes. Friction and wear behaviour of zinc dialkyl-dithiophosphate additives. *Trib Trans* 43(3):469–479, 2000.
33. U.S. Patents 2,124,598 (1938, Standard Oil); 2,156,265 (1939, Standard Oil); 2,153,482 (1939, Lubrizol); 2,178,513 (1939, Lubrizol).
34. L Tocci. Under pressure. *Lubes-n-Greases* 3:12, 20–23, 1997.
35. T Konishi, JM Perez. Properties of polyol esters—lubrication of aluminum silicon alloy. *Trib Trans* 40(3):500–506, 1997.
36. RS Gates. Boundary lubrication of silicon nitride by oxygen containing compounds. PhD thesis, The Pennsylvania State University, University Park, PA, Oct 1993.
37. JF Ford. Lubricating oil additives—a chemist's eye view. *J Inst Petr* 54:198, 1968.
38. PC Hamblin, U Kristen, D Chasen. A review: Ashless antioxidants, copper deactivators and corrosion inhibitors. Their use in lubricating oils. *Intl Colloquim on Additives for Lubricants and Operational Fluids*, WJ Bartz, ed., Techn. Akad. Esslingen, 1986.
39. JA O'Brien. Lubricating oil additives. In ER Booser, ed. *STLE Handbook of Lubrication*, Vol. II, Boca Raton, FL: CRC Press, 1984, pp 301–315.
40. JA O'Brien. Lubricating oil additives. In ER Booser, ed. *STLE Handbook of Lubrication*, Vol. II, Boca Raton, FL: CRC Press, 1984, p 309.
41. ML Doon polyglycols, foam contact agent Technical Booklet, 118-01161-592 AMS. Don Chemical Company, Midland MI, (j)
42. ML Haviland, MC Goodwin. Fuel economy improvements with friction modified engine oils in EPA and road tests. *SAE Technical Paper no.* 790945.
43. EW Dinsmore, AH Smith. Multi-functional friction modifying agents. *Lubr Eng* 20:353, 1964.
44. JH Dancy, HT Marshall, CR Oliver. Determining frictional characteristics of engine oils by engine friction and viscosity measurements. *SAE Technical Paper no.* 800364, 1980.

45. EE Klaus, EJ Tewksbury. Liquid lubricants. In ER Booser, ed., *STLE Handbook of Lubrication Vol II*. Boca Raton, FL: CRC Press, 1984, pp 229–253.
46. WG Johnston. A method to calculate pressure-viscosity coefficient from bulk properties of lubricants. *ASLE Trans* 24:232, 1981.
47. P Wu et al. The viscous behavior of polymer modified lubricating oils over a broad range of temperature and shear rate. *J Trib* 112:417, July 1990.
48. R Hoover. Flow properties and shear stability cold flow properties. In G Trotten, ed., *ASTM Manual on Fuels, Lubricants and Standards: Application and Interpretation*. ASTM, 2001.
49. *ASLE Standard Handbook of Lubrication Engineering*. JJ O'Connor, J Boyd, eds. New York: McGraw-Hill Book Co., 1968.
50. *Applications and Maintenance. Handbook of Lubrication, Vol 1*. ER Booser, ed. Boca Raton, FL: CRC Press, 1997.
51. *Theory and Design Handbook of Lubrication Vol 2*. ER Booser, ed. Boca Raton, FL: CRC Press, 1997.
52. *Monitoring of Materials Synthetic Lubricants and Applications. Handbook of Lubrication, Vol 3*. ER. Booser, ed. Boca Raton, FL: CRC Press, 1997.
53. *STLE Tribology Data Handbook*. ER Booser, ed. Boca Raton, FL: CRC Press, 1997.
54. *Synthetic Fluids and High Performance Functional Fluids*. LR Rudnick, RL Shubkin, eds. New York: Marcel Dekker, 1999.
55. *Lubricant Additives—Recent Developments*. MW Ranney, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ, 1978.
56. *Synthetic Lubricants and Additives for Lubricants—Advances Since 1977*. MW Ranney, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ, 1980.
57. *Reprocessing and Disposal of Waste Petroleum Oils*. LY Hess, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ, 1978.
58. *Proceedings, Measurements and Standards for Recycled Oils, Part I*. Spec. Publ. no. 488, NBS, Washington, DC, 1976.
59. *Recycled Oil Program, Part II*. Spec. Publ. no. 566, NBS, Washington, DC, 1977.
60. *Fuel Additives for Internal Combustion Engines 1978—Recent Developments*. MW Ranney, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ, 1978.
61. *Methanol Technology and Application in Motor Fuels*. JK Paul, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ, 1978.
62. *Ethyl Alcohol Production and Use as a Motor Fuel*. JK Paul, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ, 1979.
63. R Shaw, EE Klaus, JL Duda. Development of a bench scale test to evaluate lubricants for use in methanol-fueled engines. *Lubr Eng* 52(10):753, 1996.
64. SE Schwartz. Analysis of upper-cylinder wear with fuels containing methanol. *Lubr Eng* 42(4):292–299, 1986.
65. *Enhanced Oil Recovery—Secondary and Tertiary Methods*. MM Schumacher, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ, 1978.
66. EE Klaus et al. Generation of ultralow tension over a wide range NACN range using Penn State sulfonates. *SPE J* 73–79, 1983.
67. *Corrosion Inhibitors 1979 Recent Developments*. JS Robinson, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ, 1979.
68. *Synthetic Oils and Additives for Lubricants—Advances Since 1977*. MW Ranney, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ 1980.
69. *Boiler Fuel Additives For Pollution Reduction and Energy Savings*. RC Eliot, ed. Chemical Technology Review Series, published by Noyes Data Corp, Park Ridge, NJ., ISBN 0-8155-0729-1 (1980).

70. Lubricants World 1993, Annual Buyers Guide, Vol 3, no. 6, June 1993.
71. 1999–2000 Lubricants industry source book. Lubes-n-Greases June 15, 1999.
72. JM Perez, CS Ku, SM Hsu. High temperature liquid lubricant for advanced engines. SAE Tech. Publ. 910454, 1991.
73. JM Perez. Oxidation studies of lubricants from dornite to microreactors. In AT Riga, GH Patterson, eds., *Oxidative Behavior of Materials by Thermal Analytical Techniques*. ASTM STP 1326, 1997, p 16.
74. AA Krawetz, T Tovrog. Differential thermal analysis for estimation of the relative thermal stability of lubricants. I & EC Product Research and Development 5(2): 191–198, June 1966.
75. F Noel. The characterization of lube oils and fuel oils by DSC analysis. J Inst Petr. (London) 37(558):354–358, 1971.
76. F Noel. Thermal analysis of lubricating oils. *Thermochimica Acta* 4:377–392, 1972.
77. JA Walker, W Tsang. Application of differential scanning calorimetry to the characterization of lubricating oils. NBS Special Publication 584, Nov. 1980.
78. SM Hsu, AL Cummins. Thermogravimetric analysis of lubricants. SAE Tech Pub. 831682, 1983.
79. A Zeman et al. The DSC cell—a versatile tool to study thermooxidative degradation of lubricants and related problems. *Thermochimica Acta* 80:1–9, 1984.
80. HH Abou el Naga, AEM Salem. Testing thermal stability for base oils via thermogravimetric balance and differential thermal analyzer. *Lubr Eng* 41:470–476, 1985.
81. KF Abas, J Sadek. Characterization of fresh and used diesel engine oils by differential scanning calorimetry. *Thermochemica Acta* 126:181–185, 1988.
82. RL Blaine. Thermal analytical characterization of oils and lubricants. 18(1): 18–20, 1994.
83. Y Zhang, et al. New method to evaluate deposit forming tendency of liquid lubricants by differential scanning calorimetry, *Lubr Eng* 48(3): 189, 1992.
84. Y Zhang et al. The deposit forming tendencies of diesel engine oils—correlation between two peak method and engine tests. *Lubr Eng* 48(3):221, 1992.
85. MA Keller, CS Saba. Behavior of high temperature lubricants in pressure differential scanning calorimeter. *Trib Trans* 41(4):586–592, 1998.
86. JM Perez et al. Diesel deposit forming tendencies of lubricants—microanalysis methods. SAE Technical Paper no. 910750, Detroit, MI, 1991.
87. Annual Book of ASTM Standards, Petroleum Products, Lubricants and Fossil Fuels. American Society of Testing Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428.
88. E Citkovic, EE Klaus, F Lockwood. A thin-film test for measurement of oxidation and evaporation of ester-type lubricants. *ASLE Trans* 22:395, 1979.
89. CS Ku, P Pei, SM Hsu. A modified thin-film oxygen uptake test (TFOUT) for the evaluation of lubricant stability in ASTM Sequence IIIE. SAE Technical Paper no. 902121, Tulsa, OK, 1990.
90. DW Florkowski, TW Selby. The development of a thermo-oxidation engine oil simulation test (TEOST). SAE Technical Paper no. 932837 (1993).
91. *Friction and Wear Devices*, 2nd ed. ASLE (STLE) 834 Busse Highway, Park Ridge, IL 60068, 1976.
92. JM Perez. A review of four-ball methods for the evaluation of lubricants. *Proc ASTM Symposium on Tribology of Hydraulic Pump Stand Testing*. ASTM STP 1310, Houston, TX, 1995.
93. EE Klaus, JL Duda, KK Chao. A study of wear chemistry using a micro sample four-ball wear test. *Trib Trans* 34(3):426–432, 1991.
94. Operating instructions, PLINT TE 77 High Frequency Machine, Serial no. TE77/84 08/96 Oaklands Park, Workingham, Berkshire RG41 2FD, England.

95. JS Sheasby et al. A reciprocating wear test for evaluating boundary lubrication. *Trib Intl* 23(5): 301–307, 1990.
96. DE Weller, Jr., JM Perez. A study of the effect of chemical structure on friction and wear. Part 2—vegetable oils and esters. *Lubr Eng* 57(3);20–25, 2001.
97. ASTM Standard Test Method D4485–94. Annual Book of ASTM Standards. Petroleum Products, Lubricants and Fossil Fuels. ASTM, 100 Barr Harbor Drive, West Conshohocken, PA.
98. DJ Smolenski, RH Kabel. Effect of zinc dithiophosphate additive type on cam and lifter wear in taxi service. SAE Tech. Pub. 831,760, San Francisco, CA, 1983; SAE Spec. Tech Pub. no. 558.

Additives for Food-Grade Lubricant Applications

MICHAEL JOHN RAAB and SIBTAIN HAMID

ANDEROL Company, East Hanover, New Jersey, U.S.A.

1 HISTORICAL DEVELOPMENT

1.1 Introduction

Processing of foods and beverages into consumable products is an immense business enterprise. For instance, in the United States \$485 billion in sales revenue was generated in 1997. This makes food processing comparable in size to the transportation equipment manufacturing industry, representing nearly 13% of all manufacturing in the United States. In fact, it is larger than the entire U.S. chemical industry and is also larger than its computer equipment market. Nearly 28,000 establishments utilized a total of 1.6 million employees to create \$233 billion in value added goods [1]. Nearly \$2.8 billion of food production machinery was sold to support this market.

2 FOOD-GRADE LUBRICANTS—WHAT ARE THEY?

Food-grade lubricants are compounded or uncompounded products approved for use in meat, poultry, and other food processing equipment applications and plants. A distinction is drawn among products (1) that may come into contact with, (2) that will contact, and (3) that will never contact the foodstuff. The U.S. Department of Agriculture (USDA) originally established a rating system to control lubricants (nonfood compounds) [2] that is still in use today: H1 for use as lubricants where incidental contact might occur; H2 for use where no contact is possible; and H3 for soluble oils. H1 lubricants are generally used on equipment above the edible

product line, while H2 lubricants are used below the line. H3 lubricants are acceptable for hooks, trolleys, and similar equipment. In cases where the lubricant is used in intimate contact (say as a baking product release lubricant), the Food and Drug Administration (FDA) publishes a list of authorized ingredients in the Code of Federal Regulations (CFR) [3].

An H1 food-grade lubricant is generally composed of an approved base stock and additive(s). Maximum concentrations of each additive are also controlled. The composition of H2 lubricants is not specifically controlled but must exclude poisons, toxins, or other materials that will cause a health risk.

The following lubricant base stocks are in commercial use in or as H1 lubricants. Other uses are included for reference:

1. White mineral oil (21 CFR 172.878) may be used as a release for confectionary, bakery, dehydrated fruit, or yeast; floatation aid; components of hot-melt coating for meat; and as a dust control agent.
2. Petrolatum (21 CFR 172.880) may also be used as a release aid and as a protective coating for raw fruits and vegetables.
3. Synthetic isoparaffinic petroleum hydrocarbons (21 CFR 172.882) may be employed as a defoamer, as a component in insecticides, as a coating on shell egg, and as a floatation aid.
4. Technical white oils (21 CFR 178.3620) are authorized for use as a coating on shell eggs, as a defoamer, as a floatation aid, and as an insecticide component. Addition to food is limited to 10 parts per million.
5. Linear, random polyalkylene glycols having a number average molecular weight of 1500 or more are approved under 21 CFR 178.3570. Addition to food is limited to 10 parts per million [4].
6. Dimethylpolysiloxane with a viscosity greater than 300 centistokes or more is approved in 21 CFR 178.3570. Addition to food is limited to 1 part per million.

3 LUBRICANT ADDITIVES

The base oils described above are sometimes used directly as lubricants on operating equipment in lightly loaded and low-speed applications. However, as operating conditions become more severe, the demands on the lubricant are greatly increased. To perform under more severe conditions, the lubricant is formulated using one or more approved additives:

1. "Generally Recognized as Safe" (GRAS) for use in food
2. Used in accordance with the provisions of a prior sanction or approval
3. Contained in paragraph (a) (3) of 21 CFR 178.3570, entitled "Lubricants with Incidental Food Contact"

4 LUBRICATION IN FOOD PROCESSING: A BRIEF REGULATORY HISTORY

The processing of agricultural or animal substances into consumable food products is performed in a multifunctional manufacturing plant. Such processing includes one

or more operations such as cleansing, sterilizing, homogenizing, blending, mixing, stirring, baking, freezing, chilling, baking, frying, cooking, cutting, slicing, packaging, canning, or bottling. Large-scale food processing is often done with machinery and support components such as pumps, mixers, tanks, hoses, pipes, chain drives, and conveyer belts. Such machinery and associated support equipment contains mechanical or moving components. Hydraulic fluids, greases, gear and chain lubricants, and other oils are required to ensure reliable and efficient operation of these components.

While a good engineering design can reduce the likelihood of adulteration of the food by these lubricants, a myriad of operating constraints and tradeoffs (economic, engineering, logistics, hygienic practice, quality assurance, applicable regulations, and others) tends to increase the contamination risk. Therefore, it is essential that lubricants that may incidentally contact the food product be physiologically safe.

Formulated lubricants are based on one of five FDA approved base stock classes: white oil (various grades); synthesized hydrocarbons (polyalphaolefins, polyisobutenes); polyalkylene glycol; dimethylpolysiloxane; or natural oils.

White Mineral Oils

The Pharmacopoeia of the United States (USP) first listed “white mineral oils” in its tenth decennial revision of 1926 [4]. In 1935 a first paper presenting the general principles of white oil manufacturing can also be found. Other papers, including a text, were later published on the subject [5]. In 1950 National Formulary (NF) added “white mineral oil” to its monographs [5]. In 1965, following enactment of the Food Additives Amendment, the FDA issued regulations covering the application of Food Grade Lubricants in industrial applications.

Dimethylpolysiloxanes

Prior to 1958 no regulations covered food contact substances, or food additives in general. Some substances were allowed by their common use in food prior to 1958, and some were allowed by prior sanction letters from the FDA. One producer, Dow Corning, holds prior sanction letters for the use of dimethylpolysiloxane fluids and emulsions as defoaming agents in food processing that date back to 1953. Specific regulation covering the use of dimethylpolysiloxane in lubricants was entered in 1965 as a result of a petition filed by General Electric (GE) [6].

Hydrogenated Polyalphaolefin (PAO) Synthetic Fluids

PAOs meet all the requirements of the FDA as a white mineral oil (21 CFR 172.878); they were introduced to the market in 1981 by Gulf Research and Development Company [7].

Other Regulations and Laws

The 1958 Food Additives Amendment to the Federal Food, Drug, and Cosmetics Act created regulations covering food contact substances, or food additives generally.

Two federal laws requiring the maintenance of safe and sanitary conditions in federally inspected meat and poultry plants were then enacted. These laws are the Federal Meat Inspection Act as amended by the Wholesome Meat Act of 1967 and the Poultry Products Inspection Act as amended by the Wholesome Poultry Products Act of 1968. These acts were placed for enforcement under the Food Safety

and Quality Service through the Meat and Poultry Inspection Program (a part of the USDA). The inspection program called for authorization of substances or compounds used in processing plants [8].

Lubricants used on equipment in the processing of foods and beverages require special selection and application in order to meet the unique toxicity and sanitation needs. The USDA regulates meat and poultry plants, and the FDA monitors other food and pharmaceutical manufacturing operations.

Until 1998 the USDA [8] maintained a system of oversight by granting “prior authorization” for lubricants intended for use in food processing facilities. In September of that year, regulatory changes were imposed that affected the food-grade lubricant market of the future: the USDA Food Safety and Inspection System (FSIS) eliminated the preapproval program and implemented new regulations and procedures [9]. These regulations have shifted the burden of assessing risk. Implementation of those regulatory requirements is defined by “Hazard Analysis and Critical Control Point” procedures (HACCP). These regulations make the food processor (manufacturer) responsible for the proper selection of lubricants. However, the lubricant manufacturer and/or the equipment supplier (or OEM) still remains responsible for the composition and effectiveness of the lubricant.

HACCP requires the food processor to perform an assessment of each point in the operation at which contamination might occur. Implicit in this assessment is the need for the food processor to know and understand the physiological risk a lubricant may pose. Such an analysis may require the processor to review and approve the chemical composition of the lubricant. Prior to February 1998, the USDA performed that review role. This transfer of responsibility allows the USDA (and FSIS) to redirect its resources to ensuring the implementation of HACCP regulations.

5 FOOD-GRADE LUBRICANTS REGISTRATION: THE NEW ORDER

Commercial organizations responded to the changes in registration procedures. Notably, NSF International [10] (see www.nsf.org) and Underwriters Laboratories Inc [11] (www.ul.com) have developed programs to offer “third-party” or “external agency” certification programs.

It may interest the reader to note that the USDA/FSIS anticipated the possibility of a third-party certifier when it originally issued its intention to change the regulations. “FSIS specifically requests comments on whether an industry-recognized, non-government organization or laboratory could provide prior approval or a similar service to chemical manufacturers and distributors” [12].

In concept the approval process has changed little under the current “external agency” certification programs. These programs are based on the original USDA/FSIS “preauthorization” system. Namely, the lubricant composition is submitted to the NSF or UL along with other supporting documentation. Each component in the composition is reviewed against the U.S. FDA’s list of permitted substances (see 21 CFR Title 178). Other submitted documentation includes certifications regarding raw material sourcing and manufacturing practice(s).

Registration programs cover the original formulation by the manufacturer; amended formulation; and distributors (for authorized rebranding). Third-party registrars issue a “registration number” as a part of a registration letter for each formulation and/or rebrand. The NSF, for one, offers an Internet-based Web service

available for checking the status of registrations. The NSF maintains two types of listings on this Internet site: namely 1) products previously approved by the USDA (but not submitted to the NSF for registration); and (2) products reviewed and registered by the NSF under its applicable guidelines.

While current efforts to the third-party certifiers focus around adopting the former USDA guidelines, industry groups are at work to more rigorously define “food-grade lubricants.” These steps are the likely precursor to the development of an ISO standard; steps have already been initiated in Germany (DIN) and the United States (ANSI) in this regard. Groups such as the European Hygiene Equipment Design Group seek to evolve standards that go well beyond the current “gate-keeper” principles evolved through the former USDA guidelines. Thus, the reader can expect this area to remain in flux for the next several years.

5.1 Religious Organizations Influence Food-Grade Lubricant Composition

Several major religions further restrict the formulation of food-grade lubricants. Two are the Jewish and Muslim religions. With nearly 16 million Jews and 1.4 billion Muslims worldwide, such laws have a wide influence in the food processing industry [13]. Under both religions strict rules cover all aspects of food processing. The following paragraphs list only the portions of these dietary laws applicable to lubricants. In both religions the lubricant manufacturing plant is subject to supervision of the applicable organization.

The Jewish dietary laws are generally termed “kosher”. Approval under kosher law is done by one of several rabbinic orders. In the United States, the Orthodox Union in New York is a major approval organization. Essentially, kosher laws prohibit the use of pork and pork byproducts, and control or exclude various other materials and processes. This limitation precludes the use of lard oils and derivatives in lubricants intended for use in kosher food processing. Kosher laws also prohibit contamination of meats with dairy and eggs. All equipment must be properly cleaned, “kosherized”, and left idle for 24 hours before and after making kosher products.

The Muslim faith imposes “Halal” laws (an Arabic term meaning lawful or permitted for Muslims) on their food products. In the United States the Islamic Food and Nutrition Council of America (Chicago) issues Halal certificates. While differing in many aspects from kosher, Halal’s practical implications on lubricant formulation and production are similar. Halal excludes the use of alcohol in its products, a potential limitation for the manufacturing of some additives.

6 PATENT SEARCH—FOOD-GRADE LUBRICANT ADDITIVES

Recent applicable patents found in the preparation of this work are given as follows:

1. U.S. Patent 5,102,567 to Wolf issued April 17, 1992: High performance food-grade lubricating oil.

Abstract: An improved high-performance food-grade lubricating oil is provided that effectively lubricates bearings, gears, and slide mechanisms present in food industry equipment. The food-grade oil provides superior oxidation, thermal, and hydrolytic stability properties and is economic to manufacture. In the preferred

form, the lubricating oil includes a base oil and an additive package comprising the combination of phenolic and aromatic amine antioxidants.

2. U.S. Patent 5,380,469 to Flider issued January 10, 1995: Polyglycerol esters as functional fluids and functional fluid modifiers.

Abstract: High-viscosity functional fluids prepared by reacting a polyglycerol with a triglyceride oil or fat. The reaction products can be used as high-viscosity lubricants or blended with triglyceride-based functional fluids for use in mud drilling, as low-temperature lubricants, cutting fluids, hydraulic fluids, and food-grade lubricants.

3. U.S. Patent 5,614,479 to Chardon issued March 25, 1997: Corrosion inhibitor.

Abstract: A food-grade corrosion inhibitor for admixture with a food-grade petroleum-based oil is derived from an admixture of food-grade components: the corrosion inhibitor, a food-grade ketone, a food-grade ester, and imidazoline. The additive is incorporated into a lubricating component such as mineral oil, etc.

4. U.S. Patent 5,158,694 to Waynick issued October 27, 1992: Railroad grease.

Abstract: A high-performance, environmentally compatible railroad grease effectively lubricates railroad tracks and wheels of railway cars in compliance with environmental rules and regulations. Advantageously, the novel railroad grease is safe for plant life and animals as well as for fish in underground aquifers and nearby streams. The railroad grease desirably comprises a special adhesive polymer and an extreme-pressure, antiwear additive package, preferably a food-grade additive package, comprising carbonates combined with sulfates or phosphates.

5. U.S. Patent 5,510,392 to Feuston et al. issued April 23, 1996: Polyalpha olefins for food and pharmaceutical applications.

Abstract: A synthetic hydrocarbon-based material for direct use in foods and Pharmaceuticals which includes a hydrogenated oligomer of an alpha olefin having 5 to 20 carbon atoms.

6. U.S. Patent 5,538,654 to Lawate et al. issued July 23, 1996: Environmental friendly food-grade lubricants from edible triglycerides containing FDA approved additives.

Abstract: A food-grade lubricant composition is described that is useful as hydraulic oil, gear oil, and compressor oil for equipment in the food service industry. This composition comprises a major amount of a genetically modified vegetable oil and a minor amount of a performance additive. In other embodiments the composition contains either a phosphorus compound or a nongenetically modified vegetable oil.

7. U.S. Patent 5,578,557 to Dougan et al. issued November 26, 1996: Food-grade compressor oil.

Abstract: A food-grade compressor oil for use in a high-pressure compressor includes a base oil, an N-acyl derivative of the amino acid sarcosine, an imidazoline, and an amine-phosphate. Each of the three additives comprises no more than 0.5% by weight of the oil composition and results in high lubricity and very low corrosion even when water is present in the oil. The compressor oil may also

include polybutene, which serves as a thickener, and an antioxidant. The compressor oil of this invention is particularly well suited for use in a hypercompressor used in the manufacture of polyethylene.

8. U.S. Patent 5,639,720 to Antika et al. issued June 17, 1997: Anti-staining gear oils with low stray misting properties.

Abstract: The stray misting property of anti-staining gear oil is reduced by adding to the gear oil from about 0.1 to 5 wt% polyisobutylene of about 37,000 to 140,000 Flory molecular weight.

9. U.S. Patent 5,641,740 to Debska-Chwaja issued June 24, 1997: Lubricating oil having lubrication condition responsive activity.

Abstract: An oil particularly suited for equipment having copper containing alloy elements is compounded from about 20 to 99.75% by weight of natural or synthetic oil, and about 0.25 to 30% by weight of an acid-forming friction modifier, particularly, a fully esterified compound, such as glycerol trioleate (GTO). The oil evidences a marked improvement in frictional behavior and wear protection, especially regarding the corrosive wear of Cu-based alloys. The oil containing glycerol trioleate does not release oleic acid unless and until boundary conditions are present, thereby on the one hand effectively lubricating under boundary conditions, while on the other hand minimizing the presence of oleic acid and thus reducing chemical wear.

10. U.S. Patent 5,869,436 to Lindman issued February 9, 1999: Non-toxic antimicrobial lubricant.

Abstract: Nontoxic antimicrobial-boundary lubricant comprises a major portion of mineral oil and a minor portion of an extreme-pressure additive; an antioxidant; and an antimicrobial compound. The lubricant has a pH of about 7.4 and preferably contains chlorhexidine gluconate as an antimicrobial compound.

11. U.S. Patent 6,087,308 to Butler et al issued July 11, 2000: Non-sludging, high temperature resistant food compatible lubricant for food processing machinery.

Abstract: Lubricating oil suitable for machinery that may come into incidental contact with food is described, which contains a food-grade base oil and a combination of food-grade additives including a thickener, an antioxidant, a rust inhibitor, an antiwear additive, an antifoamant, optionally a metal passivator, and a 0.2 wt% or less coupling agent. The lubricating oil exhibits good resistance to wear, oxidation, and rust and reduced sludging at equipment surface temperatures of about 200°F and higher.

12. U.S. Patent 6,090,761 to Butler et al. issued July 18, 2000: Non-sludging, high temperature resistant food compatible lubricant for food processing machinery.

Abstract: A lubricating oil suitable for machinery that may come into incidental contact with food is described. It contains a food-grade base oil and a combination of food-grade additives including a thickener, an antioxidant, a rust inhibitor, an antiwear additive, an antifoamant, optionally a metal passivator, and a combination of up to 2.5 wt% emulsifier and coupling agent. The lubricating oil exhibits good resistance to wear, oxidation, and rust and reduced sludging at equipment surface temperatures of about 200°F and higher.

7 CHEMISTRY

7.1 General Product Structures/Classes of Materials

Five primary base stock classes are currently on the FDA's list of approved base stocks for application where there is a possibility of incidental food contact of the lubricant: white mineral oils (including petrolatum); synthetic hydrocarbons (polyalphaolefins); polyalkylene glycol; silicones; and select vegetable oils and various related derivatives.

The following general classes of additives are utilized to enhance the properties or stabilize these base materials.

7.1.1 Antioxidants

In most environments where lubricants are used, they come in contact with air, often at high temperatures and in the presence of metals or chemical contaminants, which act as pro-oxidants or catalysts. Under such conditions the lubricant undergoes a series of complex oxidation reactions. The result of this process includes an increase in the viscosity and the development of acidic contaminants and formation of carbonaceous matter. The oxidation of lubricating oils involves a chain reaction with initial formation of organic peroxides, which attack the base fluid, and then subsequent reactions with oxygen in the air continue and repeat such an attack.

The general classes of antioxidants employed to reduce organic peroxide formation are phosphites, amines, and phenols. The following list of antioxidants has been used in food-grade lubricants.

Hindered phenols: suitable phenolic antioxidants include sterically hindered phenols and thiophenols, hindered 4-hydroxy and 4-thiobenzoic acid esters, and dithioesters and hindered bis (4-hydroxy and 4-thiobenzoic acid and dithio acid) alkylene esters. Example of useful phenols include

2,6-di-tertiary-butyl phenol
2,6-di-tertiary-butyl-p-cresol
2,6-di-tertiary amyl-p-cresol
butylated hydroxy toluene (BHT)

Amines: suitable aminic antioxidants include the food-grade oil-soluble aromatic amines generally represented by phenyl naphthyl amines, alkylated phenyl naphthyl amine, diphenyl amines, alkylated diphenyl amines, and *N, N*-dialkyl phenylene diamines. Examples of suitable aromatic amines are

N-phenyl-alpha-naphthylamine
N-*p*-methyl phenyl-alpha naphthylamine
di sec butyl diphenyl amine
di-tertiary-octyl diphenyl amine
butyl octyl diphenyl amine

Phosphites such as:

tris (2,4-di-tertiary-butyl phenyl) phosphite

7.1.2 Extreme-Pressure Agents

These are chemicals added to the lubricants to prevent or minimize metal-to-metal contact. Base fluids such as mineral oil or synthetic hydrocarbons provide good lubrication as long as the lubricant film is maintained between moving parts. This kind of hydrodynamic lubrication is mainly dependent on the viscosity of the oil. When lubrication film is broken due to pressure, high temperature and velocity, a chemical compound is needed to react with the metal surfaces and form a protective coating. This type of lubrication is termed “boundary lubrication”. Under boundary lubrication conditions these chemical compounds form an adherent film of metallic salts which have a lower shear strength than that of the metal surfaces. Most of the additives used in this category are organic compounds that contain one or more elements, such as phosphorous and sulfur. Examples of extreme pressure agents include amine phosphates and triphenyl phosphorothionate, also referred to as TPPT.

7.1.3 Corrosion and Rust Inhibitors

Corrosion and rust inhibitors are chemical compounds that protect nonferrous and ferrous metals from corrosion and rusting. The chemical compounds that have been widely used in food-grade lubricants are fatty acids and their esters. Thus, esters of sorbitan, glycerol, and other polyhydric alcohols and polyalkylene glycols may be used. Food-grade esters from fatty alcohols alkoxylated with alkylene oxides or sorbitan alkoxylated with alkylene oxides or succinic acid or succinic anhydride formed by fatty acids and amines are also useful. Examples of rust/corrosion additives include

- Sorbitan mono-oleate
- Glycerol mono-oleate
- Glycerol dioleate
- Glycerol mono stearate
- Oleyl sarcosine disodium sebacate

7.1.4 Metal Deactivators

Chemical compounds used in lubricants to inhibit corrosion of nonferrous metals are known as metal deactivators. These compounds form a protective film and inhibit the reaction of sulfur compounds with metals such as copper, bronze etc. Examples of metal deactivators include derivatives of aryl triazoles.

7.1.5 Viscosity Index Improvers

Viscosity index improvers are polymers added to lubricating oils to help maintain viscosity at operating temperatures. Most of these compounds are oil-soluble polymers, which usually exert a greater thickening effect on oil at higher temperatures than at lower temperatures. The result of such thickening is that the lubricant suffers less viscosity change with changing temperatures. Examples of viscosity index improvers include polyisobutylene and high-molecular-weight decene polymers.

7.1.6 Lubricity Agents

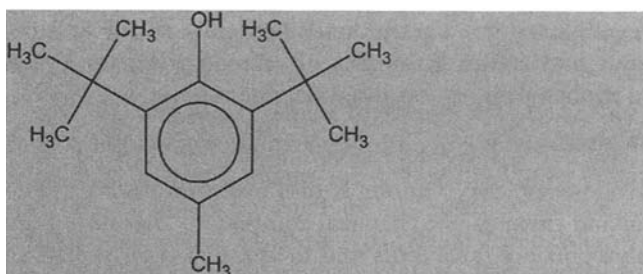
Lubricity additives in food-grade lubricants are chemical compounds that are relatively polar compared to the mineral oil or polyalphaolefins, such as glycerol mono-oleate, glycerol di-oleate, glycerol mono stearate, lecithin, oleic acid, lard oils, and other oleic acid esters.

7.1.7 Antifoam Agents

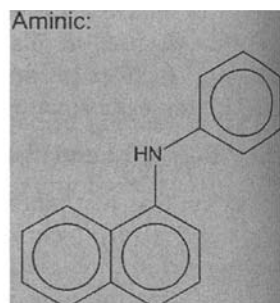
Some lubricating oils have an inherent tendency to cause foaming, especially when they are additized and contain polymeric materials. These high-viscosity lubricants take a longer time to release air from them. To overcome this problem silicones are used, which have a viscosity greater than 300 cSt at 40°C, such as dimethyl siloxane.

7.2 Structures of Additives

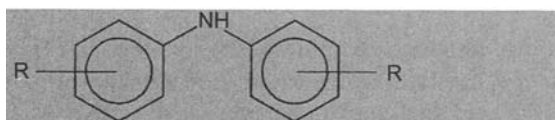
Antioxidants: Hindered phenols



butylated hydroxy toluene (BHT) or 2,6-di-*t*-butyl 4-methyl phen-1-ol



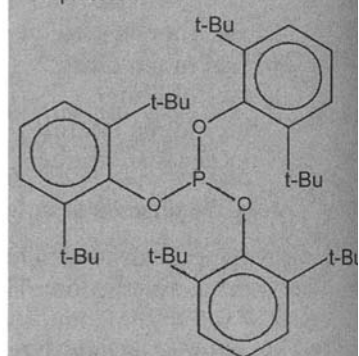
N-phenyl- α -naphthylamine



Alkylated diphenylamine

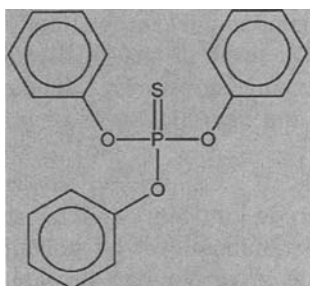
Where R is typically a tertiary butyl or an iso-octyl moiety.

Phosphites:



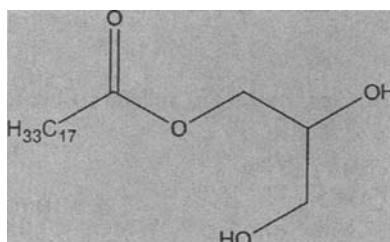
tris-(2,6-di-*t*-butyl phenyl) phosphite

Antiwear/extreme-Pressure Agents: tri-phenyl phosphorithionate (TPPT)

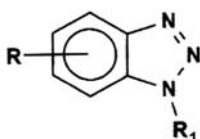


tri-phenyl phosphorithionate (TPPT)

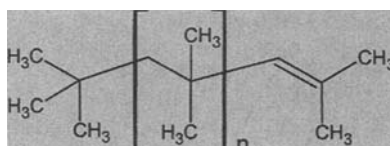
Corrosion inhibitors: glycerol mono oleate



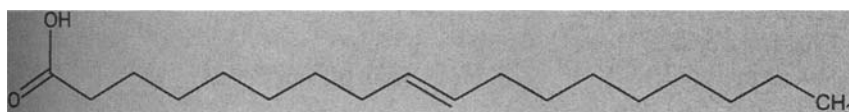
Metal deactivators: aryl triazole where R may be H and/or alkyl and R₁ may be H, alkyl, aryl, alkyl amine, or an aryl amine moiety.



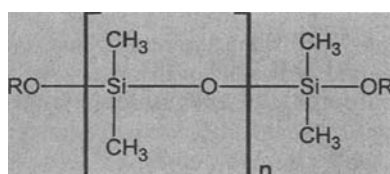
Viscosity improvers: Polyisobutylene



Lubricity agents: Oleic acid, C18 : 1



Antifoam agents: Polysiloxane where R may be H, methyl or an alkyl group



7.3 Current Commercial Routes

Chemical structures indicated in (1)–(5) are commercially available from reputable companies in the United States and Europe.

8 PROPERTIES AND PERFORMANCE CHARACTERISTICS

8.1 C-1 Chemical and Physical Properties

8.1.1 Diphenyl Amine

Appearance	Clear, viscous, yellow to brown liquid
Viscosity at 40°C	276 cSt
Density at 20°C	0.97 g/cm ³
Flash point, °C	185
Solubility:	Mineral oil, 5% Water, <0.01

8.1.2 Triphenyl Phosphorothionate

Appearance	Gray or yellow powder
Melting point, °C	51–54
Phosphorus content	8–10%
Acid number	0.03 mg KOH/g

8.1.3 Glycerol Mono Oleate

Appearance	Clear liquid
Flash point, °C	242
Viscosity, °C	10.0 cSt
Density, g/l at 15.6°C	948
Acid number	6.0

8.1.4 *N*-acyl Derivative of the Amino Acid Sarcosine

Appearance	Dark amber liquid
Viscosity at 40°C	660 cSt
Specific gravity 20°C	0.98
Free fatty acid	6.00%
Solubility	Soluble in mineral oil/PAO

8.1.5 A Typical Aryl Triazole Derivative

Appearance	Brown liquid
Viscosity at 40°C	83 cSt
Density at 25°C	7.9 lb/gal
Flash point, °C	>150 (COC)
Solubility	Soluble in mineral and synthetic oils

8.1.6 Polyisobutylene

Appearance	Clear, light yellow viscous liquid
Pour point, °C	+15 to –40
Viscosity at 40°C	35,000 to 140,000
Fire point, °C	230 min
Density, lbs/gal	7.2 to 7.5

8.1.7 Oleic Acid

Appearance	Colorless to pale red
Freezing or Melting point, °C	16.3
Molecular Weight	282.2
Viscosity at 25°C, mPa.s	25
Flash Point, °C	180
Density, lbs/gal	7.24

8.1.8 Polydimethylsiloxane

Appearance	Crystal clear liquid
Pour point, °C	−50 to −70
Melt Point, °C	−41 to −25
Viscosity at 40°C, cSt	50 to 100,000
Flash Point, °C	>318
Specific gravity at 25°C	0.96 to 0.97

Acknowledgement

Chemical structures originally drawn using ACD Labs (Toronto, Canada) Chem-Sketch 4.0 Software Program.

REFERENCES

1. 1997 Economic Census Data, NAICS group 311 and 3121 (excluding tobacco manufacturing). See also EC97M series reports: 3111A through 3121F.
2. USDA, FSIS Miscellaneous Publication 1419 (updated yearly until 1998), List of proprietary substances and nonfood compounds.
3. *Code of Federal Regulations*, Vol 21, Parts 170 to 199, revised annually, U.S. Government Printing Office, Washington, DC or at [at//frwebgate.access.gpo.gov](http://frwebgate.access.gpo.gov).
4. Private correspondence with USP. In it, USP traces the monogram of petrolatum, mineral oil, white mineraloil and other items, April 6, 2001.
5. R. Morawek, Tietze, Rhodes. *Food grade lubricants and their applications*. Presented to American Society of Lubrication Engineers (now STLE), 33rd Annual Meeting in Dearborn, MI. April 17–20, 1978.
6. A private correspondence between Dow Corning (D. Como and J. McCourt) and the author, April 23, 2001.
7. RD Galli, BL Cupples, RE Rutherford. *A new synthetic food grade white oil*. Presented at the 36th Annual Meeting of the Society of Tribologists and Lubrication Engineers (STLE) in Pittsburgh, PA, May 11–14. 1981.
8. USDA, Food Safety and Quality Service, Agriculture Handbook No. 562, Guidelines for obtaining authorization of compounds to be used in meat and poultry plants, Sept. 1979.
9. MJ Raab, *Assuring food safety in food processing: The future regulatory environment for food-grade lubricants*. Presented at the 55th Annual Meeting of STLE on May 8, 2000.
10. *NSF Registration Program for Proprietary Substances and Nonfood Compounds Used in USDA Meat and Poultry Facilities*, Version 1.0, January 24, 2000.
11. *UL Recognized Component Program*, private correspondence with the author, 1999.
12. *Elimination of prior approval for proprietary substances and nonfood compounds* (Docket 91-007N), *Federal Register* 63, 7319–7322, Feb. 13, 1998.
13. Kosher vs. Halal—a Simplified comparison for the food professionals. The Islamic Food and Nutrition Council of America, undated.

Lubricant Additives for Magnetic Recording Disk Drives

THOMAS E. KARIS

IBM Research Division, Almaden Research Center, San Jose, California U.S.A.

H. S. NAGARAJ

IBM Storage Systems Division, San Jose, California U.S.A.

1 SUMMARY

This chapter reviews stability enhancement of hydrocarbon oils and perfluoropolyethers to meet the demands of advanced magnetic recording hard disk drives. Chemical degradation mechanisms are developed to provide guidelines for additive selection and interpretation of the test results. The focus is on the analytical tools employed to optimize an additives system for oil stabilization in the presence of catalytic bearing metals. Analytical tools and accelerated test methods are demonstrated through examples of their use in developing an ultrastable grease formulation.

2 INTRODUCTION

Evolutionary improvements in magnetic recording disk drive technology are achieved by a conjunction of science, engineering, and precision manufacturing [1,2]. The basic components of a disk drive have changed little over the past decade. A disk drive comprises one or more rotating disks, coated with a thin magnetic film, and mounted on a rotating spindle motor. These components are schematically shown in [Figure 1a](#). A magnetic recording head stack assembly writes and reads data as magnetic flux transitions on the disk surfaces. Drive electronics coordinate the actuation of the head stack assembly and data transfer. Lower cost per bit of stored data, higher data density, and increased data transfer rates have been accomplished,

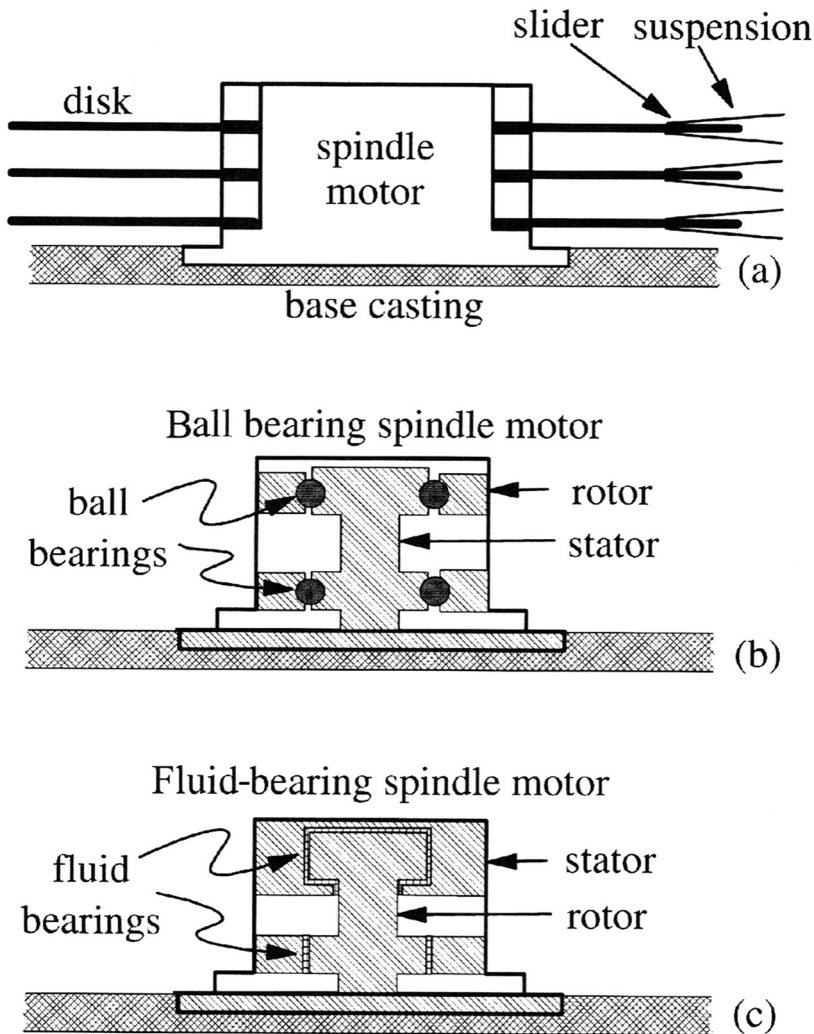


Figure 1 Schematic illustration of the disk pack on the spindle motor with the head suspension assembly (a), a ball bearing spindle motor (b), and a fluid-bearing spindle motor (c).

in part, by increasing the disk rotation rate, lowering the nonrepeatable run out of the spindle motor, and reducing the spacing between the magnetic recording heads and the disk surface.

Lubrication plays a vital role in the spindle motor and at the head disk interface. Spindle motors are schematically shown in Figure 1b and c. Coil windings and magnets are not shown. Disks are mounted on the outer hub, or rotor, separated by spacer rings. In this design, the stator is bolted to the base casting of the disk drive enclosure. Presently, the vast majority of disk drives on the market contain ball bearing spindle motors (Figure 1b). Here, the rotor and stator are joined by ball in cage rolling element bearings lubricated with channeling grease. Within the past decade,

rotation rates increased from 3,600 rpm to 10,000 rpm. This increase in rotation rate with steel ball bearings was enabled by enhanced grease stability through the use of lubricant additives.

One limitation of the present ball bearing motors is their nonrepeatable runout, which constrains the track density relative to the performance of the track following servomechanism [3]. A fluid-bearing motor is presently under development to allow further increases the data recording track density [4-6]. The fluid-bearing motor (Figure 1c) provides a lower nonrepeatable runout [7,8]. In the fluid bearing, a several micron-thick film of oil lubricates the relative motion between the rotor and stator. Radial and axial stiffness are provided by thrust grooves machined into the bearing surfaces, which also confine the oil within the gap. While the fluid bearing operates mostly in the hydrodynamic lubrication regime, it passes through the boundary lubrication regime during start/stop operations. Lubricant additives are needed to control oil oxidation and to improve boundary lubrication performance. Antistatic additives are needed in fluid-bearing motor oil to prevent charge buildup across the oil-filled bearing gap, which acts as a capacitor. Electrostatic potential may influence the magnetic recording head disk interface tribology [9,10].

Nano-scale dimensions and high relative velocity are routinely encountered in the head disk interface. The carbon overcoat, lubricant, and the air bearing gap at the head disk interface are compared with a typical virus and the mean free path of air under atmospheric pressure, about 100 nm, in Figure 2. The air bearing gap, referred to as the "flying height," in modern disk drives is on the order of 20 nm. Plans within the industry are to reduce this spacing to 10nm or less in the near future. Tribology of the head disk interface has been the focus of unprecedented industrial and academic research, rivaled only by miniaturization efforts in the semiconductor industry. For all this expenditure, there are relatively few choices of disk lubricants and additives. Lubricant is needed to prevent wear during intermittent asperity contacts. Additives have been investigated to enhance perfluoropolyether disk lubricant performance.

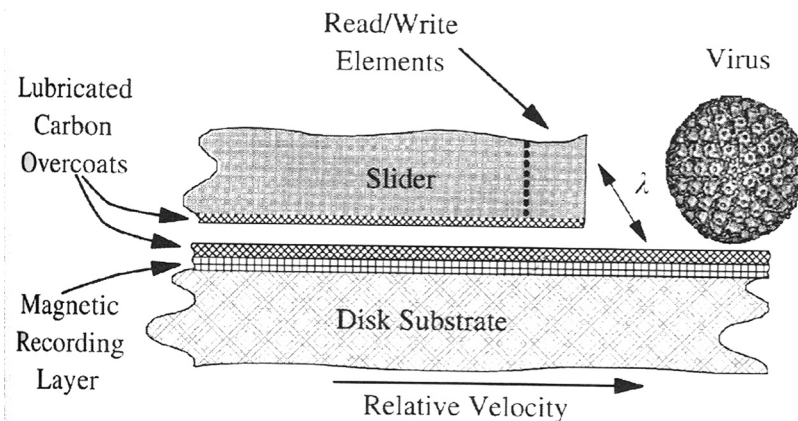


Figure 2 A schematic of the head disk interface, with the interface layers, air gap, mean free path of air λ , and a typical virus, drawn to scale.

3 LUBRICANTS

3.1 Ball Bearing

Ball bearing spindle motor bearings are typically lubricated with an NLGI grade-2 lithium grease. The grease comprises 10wt % lithium 12-hydroxy stearate thickener, and the oil is a blend of 76.9 wt % tetraester oil, 19.2wt % diester oil, with 2.2 wt % of a primary antioxidant, and 1.7 wt % of an antirust additive. Lithium soap fibers thicken the grease [11]. The oil viscosity at 40°C is 26 centistokes, and the worked penetration is 245. Other types of hydrocarbon greases with polyurea thickener, or perfluoropolyether greases thickened by tetrafluoroethylene telomer particles, are unacceptable for disk drive bearings due to torque spikes produced by mashing of the thickener at the ball-race interface [12].

The single primary antioxidant previously incorporated in the bearing grease was barely adequate to provide shelf-life stabilization. After several years of storage at ambient conditions, the lithium grease, which initially appeared as a translucent milky white gel, had turned brownish, and chemical analysis revealed that the antioxidant had been depleted. Similar findings are reported in [13]. Accelerated bearing life tests demonstrated an unacceptable failure rate at mildly elevated temperatures and 10,000 rpm (Figure 3). Oil is lost from the bearing, as shown in Figure 3a. The medium anderson, shown in Figure 3b, is a measure of irregularities that occur from 10 to 60 times per rotation of the inner race (Precision Devices, Inc., 606 Country Street, PO Box 220, Milan, MI 48160-0220). Chemical analysis of the grease, bearings, and oil from this test indicated that the bearing failure was due to metal catalyzed oxidation of the grease oil. Grease degradation that causes rotational irregularities begins with oil oxidation [14,15].

Commercial tetraester oil was selected as a model grease oil within which to develop a stabilizing additive system. The tetraester oil was a reaction mixture of pentaerythritol with pentanoic and nonanoic acids in an approximately 80:20 molar ratio [16]. This effectively produces the mixture of oil molecules shown in Figure 4. Some chain branching is present in the actual oil but is not shown here.

3.2 Fluid Bearing

Fluid bearings are typically lubricated with synthetic ester oils. Since the motor power dissipation is critically dependent on the oil viscosity, the viscosity should be less than 10mPa-sec at 40°C. However, to limit oil evaporation from the free surface of the fluid bearing, the vapor pressure should be less than 30mPa at 100°C. Because of the relationship between vapor pressure and viscosity, presently used oils provide the best compromise between these two properties. Most of the published information about fluid bearing oils is in the patent literature. Coant et al. [17] disclose mixtures of ester oils with a metal-containing detergent, a friction reducer, and an antioxidant. Nebzydoski et al. [18] disclose ester oils containing aromatic amine antioxidants, aryl phosphate esters, and an amine salt of *N*-triazolyl-hydrocarbyl succinamic acid. Metro et al. [19] disclose ester oil containing a phosphate ester and an alkyl amine. Ohno et al. [20] disclose a fluid-bearing apparatus using a trimethylol propane ester lubricant. Modern fluid-bearing spindle motors typically contain neopentyl glycol ester oil.

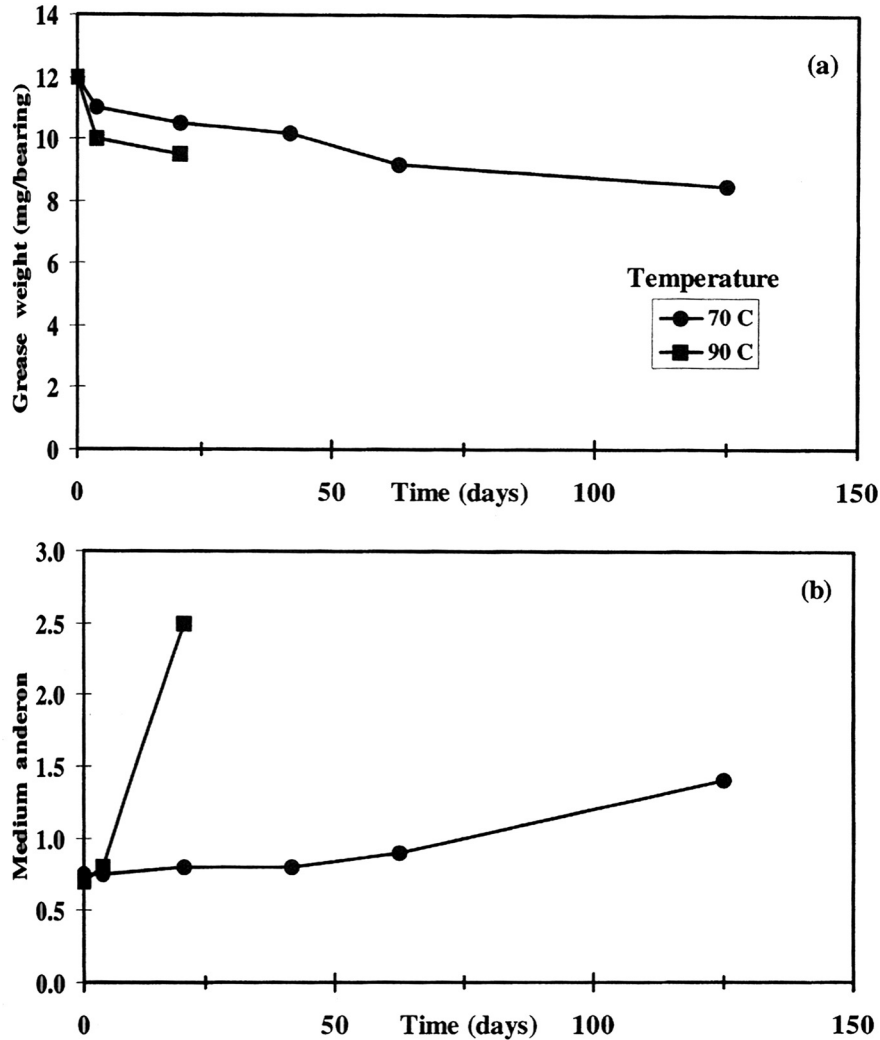


Figure 3 Accelerated disk drive spindle motor bearing life test with commercial lithium grease, 5×13 bearings, 19.6 N preload, 10,000 rpm, grease weight loss, and medium anderson versus run time at 70 and 90°C.

Commercial diester and hydrocarbon oils selected as model fluid-bearing oils within which to develop a stabilizing antioxidant system and conductivity additives are listed in [Table 1](#).

3.3 Magnetic Recording Disk

Head disk interface air bearings are most often lubricated with functional perfluoropolyethers. Some of the fluorocarbon oils considered for use as magnetic recording disk lubricants are shown in [Table 2](#). The most widely used magnetic recording disk

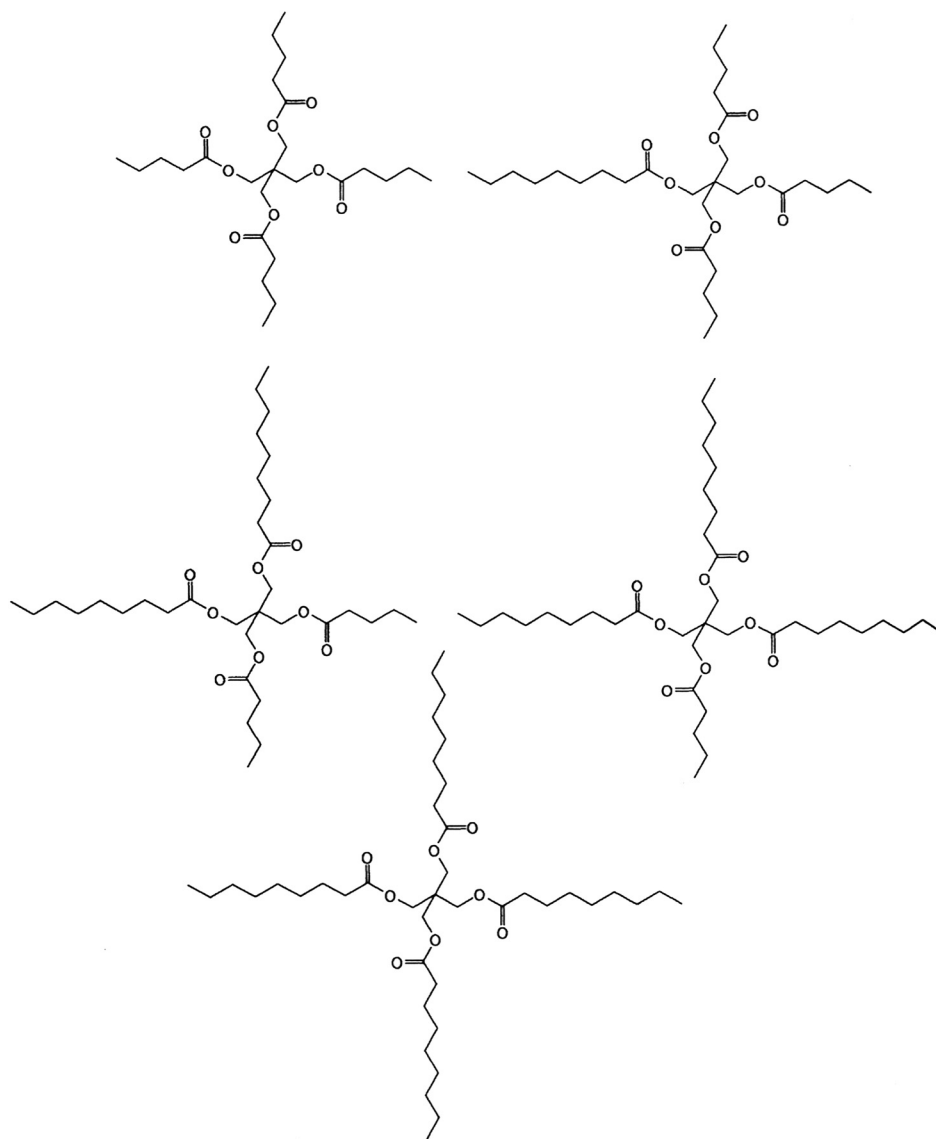
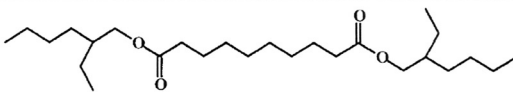
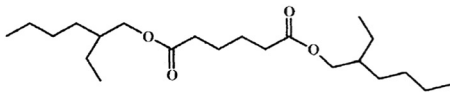
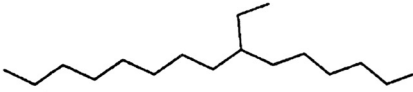


Figure 4 The model tetraester oil used to develop the spindle motor bearing grease additives system.

lubricant is Zdol 4000, with composition $0.492 < m < 0.612$, $0.383 < n < 0.526$, $p, q < 0.005$, and degree of polymerization $39 < x_0 < 46$. The perfluoropolyethers have physical properties that are distinctly different from those of hydrocarbon oils. The surface energy [21] and cohesive energy density [22] of perfluoropolyethers like Zdol 4000 are less than those of comparable hydrocarbon ethers. Chemi- and physisorption of the polar hydroxyl end groups of Zdol onto the carbon overcoated surface of the disk influence the tribological performance of the interface [23].

Table 1 Model Fluid Bearing Oils Employed for Additive System Development

Additive	Molecular weight (g/mol)	Structure
DOS	426	
DOA	370	
PAO	240	

DOS, di 2-ethylhexyl sebacate, DOA, di 2-ethylhexyl adipate, and PAO, poly alpha olefin. The PAO structure is consistent with proton NMR measurements on the sample used for this study. The PAO sample may comprise a mixture of oligomers.

Table 2 Typical Magnetic Recording Disk Lubricants with a Perfluoropolyether Fomblin Z-type Backbone Chain and Different Types of End Groups

Backbone chain	
$\text{E}-\text{O}-\left[\text{CF}_2\text{O} \right]_m \left[\text{CF}_2\text{CF}_2\text{O} \right]_n \left[\text{CF}_2\text{CF}_2\text{CF}_2\text{O} \right]_p \left[\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O} \right]_q \text{E}$ <div style="text-align: right;">x_0</div>	
Abbreviation	End group, E
Z	—CF_3
Zdiac	$\text{—CF}_2\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{—OH}$
Zdecal	$\text{—CF}_2\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{—O—CH}_3$
Ztetraol	$\text{—CF}_2\text{CH}_2\text{—O—CH}_2\overset{\text{OH}}{\underset{ }{\text{CH}}}\text{—CH}_2\text{—OH}$
Zdol-TX	$\text{—CF}_2\text{CH}_2\text{—}\left(\text{OCH}_2\text{CH}_2 \right)_{1.5}\text{—OH}$
Zdol	$\text{—CF}_2\text{CH}_2\text{—OH}$

Note: *m*, *n*, *p*, and *q* denote the chain composition, and *x*₀ is the degree of polymerization.

4 DEGRADATION MECHANISM

4.1 Hydrocarbon Oil

A chemical reaction mechanism was established to guide the additives selection and the interpretation of the chemical analysis test results. Figure 5 illustrates the hydrocarbon oil oxidation mechanism [24]. First, a carbon radical $R\cdot$ is formed: thermally at high temperature or mechanochemically in a sliding interface. The first radical gives rise to at least three new carbon radicals. This is chain propagation (indicated by the curved arrows leading to the radical at the top of the chain).

The carbon radical reacts with oxygen to form a peroxy radical $R-O-O\cdot$. The $R-H$ written alongside the arrows represents the hydrocarbon chains of the oil.

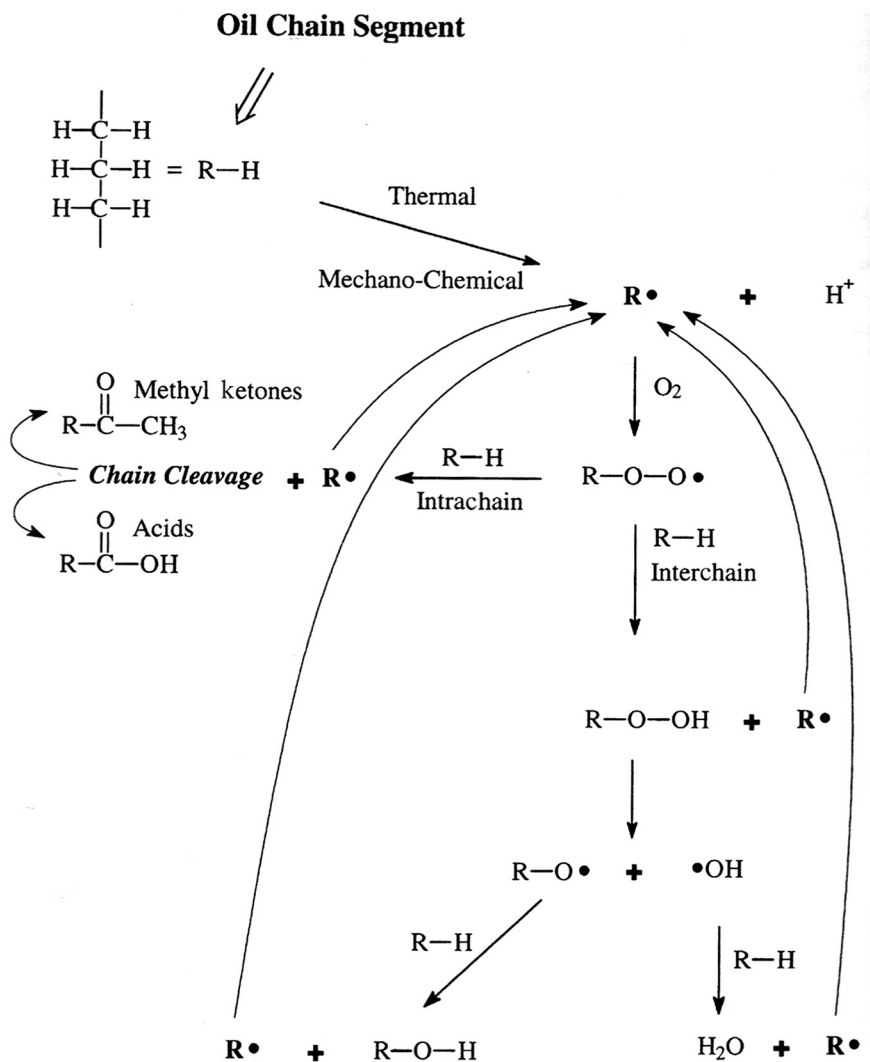


Figure 5 Oxidation of hydrocarbon oil.

The oxidation products are present only in trace amounts throughout most of the test. The peroxy radical can abstract an adjacent proton from the same chain it is on (intrachain). This produces a new carbon radical and leads to more products including chain cleavage. Chain cleavage forms shorter chains with methyl ketone or acid end groups. The acids begin to dissolve the bearing metal. Returning to the peroxy radical—it can also abstract a proton from another oil chain (interchain), leading to a different series of products. This produces a new carbon radical and a hydroperoxide $R-O-OH$. The hydroperoxide decomposes into an alkoxy radical $R-O\cdot$ and a hydroxy radical $\cdot OH$. The hydroxy radical abstracts a chain proton, which forms a new carbon radical and water. The alkoxy radical abstracts a proton, which forms a new carbon radical and leaves a hydroxyl group $R-O-H$ on the original oil chain.

Acidic oxidation products dissolve trace amounts of bearing metal (M) into the oil. Dissolved iron and chromium catalyze the decomposition and formation of hydroperoxide, according to the reduction-oxidation shuttle mechanism shown in [Figure 6](#) [25,26]. Dissolved catalytic metal greatly increases the oxidation rate.

Oxidation is inhibited by antioxidant (AOX). Primary AOX protonates the radicals [27], and secondary AOX decomposes peroxides [28], as shown in [Figure 7](#). Even though most of the radicals are quenched by the antioxidant, a small but finite amount of oxidation continues. The oxidation products include carboxylic acids. Carboxylic acids dissolve catalytic metal ions into the oil. A small amount of catalytic metal is still dissolved when antioxidants alone are used. Metal passivator, such as TCP, [29] along with the antioxidants moderates the metal dissolution. The combination of primary and secondary antioxidant, and metal passivator, should provide a "synergistic" stabilization of the oil in the presence of catalytic metal-baring surfaces.

4.2 Disk Lubricant

Disk lubricant is present as a molecularly thin film, 1 to 2 nm thick. In the case of Zdol, the hydroxyl end groups are physi- or chemisorbed onto the carbon overcoats. An asperity contact between the slider and the disk, with relative velocity of 10 to 30 m/sec, is depicted in [Figure 8](#). When a Zdol chain is subjected to a several μ sec stress/strain impulse in an asperity contact, the bond lengths and angles are strained, because the time scale of the asperity contact is shorter than the rheological time scales for flow in the confined film. During the time between the asperity contact and the onset of energy dissipation, there is an increased probability of chain scission, or bond dissociation. The probability of bond dissociation is increased if the chain is on a catalytic surface. The probability of bond dissociation also appears to be increased when chain ends are strongly tethered to the overcoat by chemisorption, or to a lesser degree, weakly tethered by the absence of interposed water on surface sites. The result is that increasing the degree of chemisorption, or decreasing the relative humidity, increases the Zdol degradation rate [23].

5 ADDITIVES

5.1 Hydrocarbon Oil

Primary antioxidants are listed in [Table 3](#), in order of decreasing molecular weight. Both hindered phenols and secondary aromatic amine types of primary antioxidant

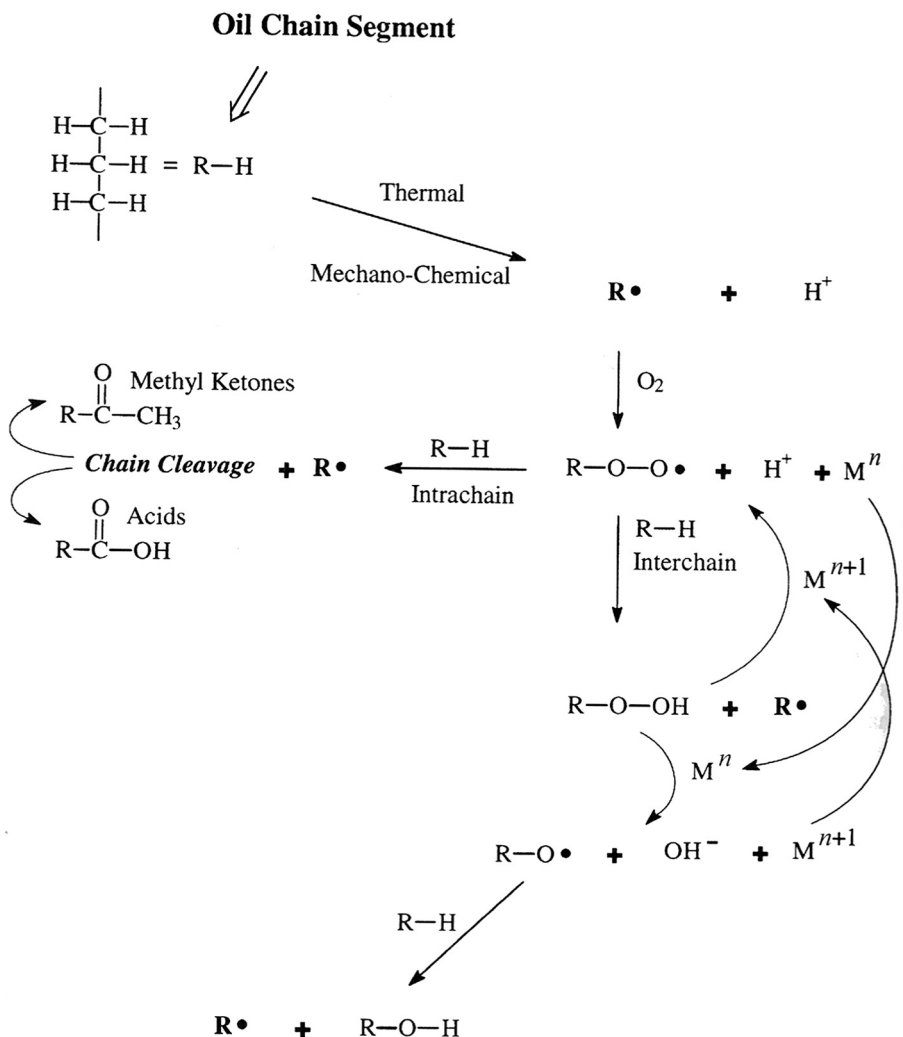


Figure 6 Metal-catalyzed oxidation of hydrocarbon oil.

are considered. The phenolic antioxidants are butylated hydroxy toluene, 4-methyl-2,6-di-tert-butyl phenol, BHT, and 4,4-methylene-bis 2,6-di-tertbutylphenol, MBDBP. Secondary aromatic amine antioxidants are octylated diphenylamine, DDA, *N*-phenyl-1-naphthylamine, PNA, and phenothiazine, PZ. A relatively new antioxidant consists of oligomers of octylated phenyl-naphthylamine and octylated diphenylamine, 50 wt % in a tetraester oil carrier, Oligomers, $x > y$, and x [30]. The oligomers concentration reported here is the concentration of the active ingredients, which is half the concentration of the commercially available reaction mixture that was formulated into the oil. Among the primary antioxidants, BHT and MBDBP are referred to as low-temperature antioxidants, and the oligomers, DDA, and PNA are referred to as high-temperature antioxidants.

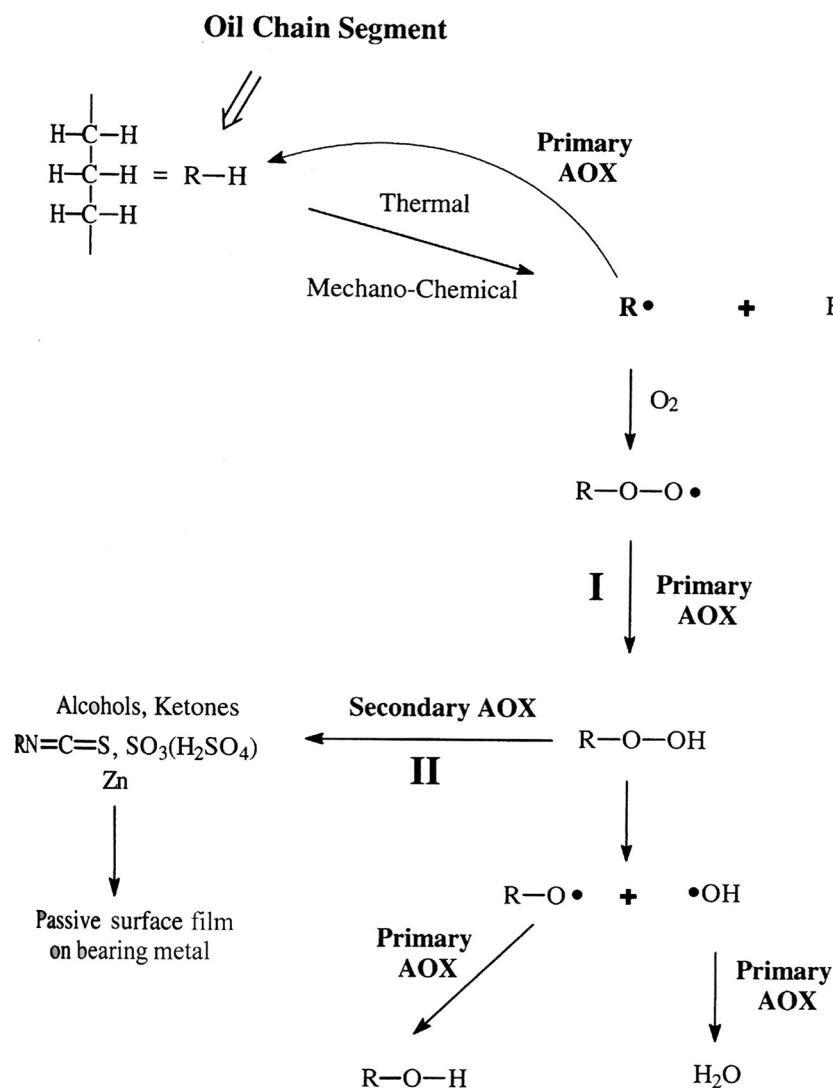


Figure 7 Stabilization of hydrocarbon oil by primary and secondary antioxidants.

Secondary antioxidants, metal passivator, and chelating agent are shown in Table 4. The zinc dialkyl dithiophosphate, ZDDP ($\text{R}=\text{branched primary C8 alkyl}$), and zinc dialkyl dithiocarbamate, ZDTC, are secondary antioxidants. The ZDTC was a zinc diamyl dithiocarbamate (*n*-pentyl or iso-pentyl) incorporated as 50 wt% ZDTC in a mineral oil carrier, or as pure ZDTC. A zinc dibutyl dithiocarbamate was also tried, but it was difficult to dissolve in the tetraester oil and formed a gellike precipitate in the early stages of oxidation. The decomposition products from the chemical reaction between ZDDP or ZDTC with hydroperoxide [31–33] form a passive film on metal surfaces, as schematically illustrated in Figure 7 [34–36].

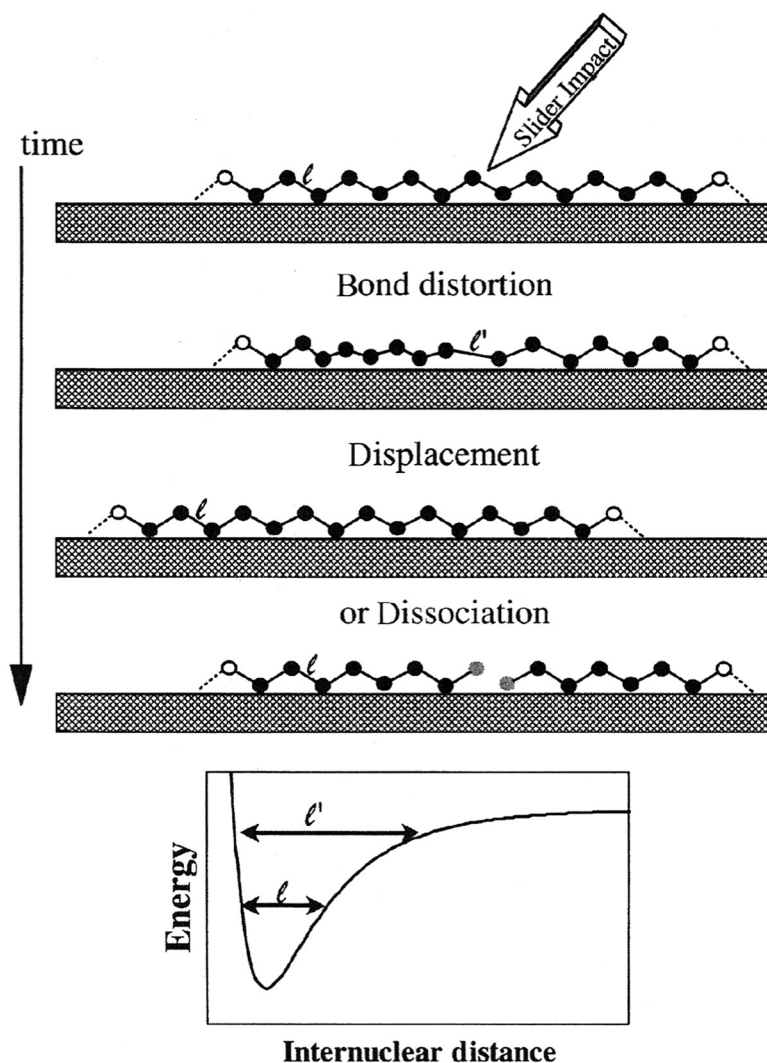


Figure 8 Mechano-chemical degradation of perfluoropolyether magnetic recording disk lubricant. The mechanical energy impulse in asperity contact increases the bond vibration amplitude l to l' which increases the probability of bond dissociation.

Tricresyl phosphate, TCP, was employed as a metal passivator in some of the accelerated aging tests. The passive film on the metal surfaces [37] inhibits the dissolution of catalytic metal ions by organic acid products of oil oxidation [38,39].

A metal chelator, *N,N'*-disalicylidene-1,2-propanediamine, DMD, was evaluated for its ability to bond with and remove dissolved metal ions from solution. The trisodium salt of *N*-(hydroxyethyl)-ethylenediaminetriacetic was also tried as a chelating agent, but it was relatively insoluble in the oil. The use of these additives in fuels and oils is reviewed in Cummings [40].

Table 3 Primary Antioxidants for Hydrocarbon Oil

Additive	Molecular weight (g/mol)	Structure
Oligomers	1397*	
MBDBP	424.66	
DDA	393.65	
BHT	220.35	
PNA	219.28	
PZ	199.27	

In order to simulate the presence of bearing metals, dissolved iron, or solid metal, was included in most of the tests on the oil. Dissolved iron was added as Fe^{3+} from iron (III) 2-ethylhexanoate. Bearing metal was included as ball bearings (304 stainless steel, 3/32-in. diameter, grade 200). For tests on the fluid-bearing oil, sintered leaded bronze filings were also included in most of the tests. The effects

Table 4 Secondary Antioxidants, Metal Passivator, and Metal Deactivator for Hydrocarbon Oil.

Additive	Molecular weight (g/mol)	Structure
ZDDP	—	
ZDTC	530.22	
TCP	368.36	
DMD	280.32	

of metal catalysis on oil oxidation have been investigated by [26,41–43] and are reviewed in [25].

5.2 Conductivity

Numerous conductivity additives for hydrocarbon oils were developed throughout the 1900s to avoid vapor ignition by electrostatic discharges during fuel transfer [44–47]. The most effective hydrocarbon conductivity additive is a mixture of a polyamine and a polysulfone, with dodecylbenzene sulfonic acid, referred to as mixed polymers in Table 5 [48]. More recently, conducting polymers, such as polyaniline, have been finding their way into novel applications such as preparation of conducting composites and adhesives. Low-molecular-weight polyaniline oligomers, PAN in Table 5, were also sufficiently soluble to employ as a conductivity additive for fluid-bearing oils [49–51]. Other types of conductivity additives have also been developed for fluid-bearing motor oil [52].

Table 5 Conductivity Additives for Fluid-Bearing Oil

Additive	Structure
PAN	<p>The structure shows a repeating unit of a polyaryleneamine. It consists of a central benzene ring connected to two amine groups (-NH-). One amine group is part of a repeating unit with a long alkyl chain (C₁₂H₂₅) and a sulfonate group (-SO₃⁻). The other amine group is part of a repeating unit with a benzene ring and a sulfonate group (-SO₃⁻). The repeating units are connected by amine groups (-NH-).</p>
Mixed polymers	<p>The structure shows a repeating unit of a mixed polymer. It consists of a central benzene ring connected to two amine groups (-NH-). One amine group is part of a repeating unit with a sulfonate group (-SO₃⁻) and a hydroxyl group (-OH). The other amine group is part of a repeating unit with a sulfonate group (-SO₃⁻) and a hydroxyl group (-OH). The repeating units are connected by amine groups (-NH-).</p>
	<p>The structure shows a sulfonic acid derivative. It consists of a long alkyl chain (C₁₂H₂₅) connected to a benzene ring, which is further connected to a sulfonic acid group (-SO₃H).</p>

5.3 Disk Lubricant

Due to the relatively poor solubility of hydrocarbons in perfluoropolyethers, and the different type of degradation mechanism, there is a lean menu of additives that are potentially feasible for incorporation in the molecularly thin films of disk lubricant. Most of the additives for perfluoropolyethers focus on inhibiting heterogeneous catalysis on the surfaces. Lewis acid catalysis of perfluoropolyether chain scission is inhibited by some organic compounds, e.g., arylamines, benzimidazole derivatives, and selenium derivatives [53].

Cyclic phosphazines were initially developed to lubricate high-temperature turbine engines [54]. A cyclic phosphazene X-1P (partially fluorinated hexaphenoxycyclotriphosphazene) is thermally stable, whereas Zdol disk lubricant undergoes catalytic scission on the Lewis acid surface of ceramics at elevated temperatures in high-pressure differential scanning calorimetry [55]. The two most widely investigated disk lubricant additives are the derivatives of cyclic phosphazine shown in Table 6.

Table 6 Additives for Magnetic Recording Disk Lubricants.

Additive	Structure
X-1P	
X-100	

Addition of 1% by weight of X-1P to Z-type perfluoropolyethers prevents catalytic scission on alumina powder by passivating the catalytic sites [56], X-1P also increases the surface diffusion mobility of lubricant on the disk by mediating the polar interactions between the Zdol end groups and the overcoat [57]. Addition of X-1P to Zdol suppresses both the generation of scission fragments and desorption of oligomers [58]. X-1P alone, as well as mixtures of X-1P in Zdol, has been shown to improve start/stop durability [59,60].

In addition to cyclic phosphazines, a number of other additives are effective at inhibiting catalytic scission of perfluoropolyethers, but these have not been evaluated for use in magnetic recording. One disadvantage of most inhibitors is their low solubility in perfluoropolyethers, making them prone to phase separation and dewetting. A perfluoropolyether substituted perfluorophosphine had improved solubility in Z- and Krytox-type perfluoropolyethers and greatly improved their thermal stability in the presence of catalytic metals [61]. Several antiwear additives known to be effective for boundary lubrication in hydrocarbon oils were modified to make them soluble in perfluoropolyethers by attaching short perfluoropolyether chains onto them. These are intended to react with active sites at the surface, inhibiting the catalytic effects of metal. Additives based on phosphate, thiophosphate, β -diketone, amide/thiol, and sulfite exhibited antiwear activity during four-ball wear tests in vacuum [62].

Gschwender and Snyder [63] developed an interesting class of perfluoropolyether-soluble perfluoroalkyl diphenyl ether stabilizers, and these stabilize perfluoropolyethers in high-temperature oxidation corrosion tests. These compounds may act to stabilize perfluoropolyethers by (1) acting as free-radical traps (analogous to antioxidant in hydrocarbons), (2) reacting with oxides or fluorides that catalyze degradation, and (3) providing a physical separation between the perfluoropolyether and the wall [64].

6 ADDITIVES TESTING

6.1 Volatility

For a sufficiently long useful lifetime, the additives should be less volatile than the oil in which they are used. A measure of the relative volatility of the additives is

Table 7 The Evaporation Flux of Additive Solutions at 125°C

Composition	Sample	Evaporation flux (kg/m ² -sec $\times 10^8$)
Pure	Tetraester oil	9
	BHT	590
	PNA	24
	PZ	20
	ZDTC/mineral oil 50/50	14
5wt % in tetraester oil	DDA	Same as pure oil
	MBDBP	Same as pure oil
	Oligomers	Same as pure oil
	ZDTC	Same as pure oil
	DMD	Same as pure oil
	TCP	Same as pure oil

obtained by measuring their evaporation rates from 5% solution in the tetraester oil. Isothermal thermo gravimetric analysis (TGA) measures the weight loss as a function of time at constant temperature. A 5–10-mg sample is rapidly heated to the measurement temperature under a dry nitrogen atmosphere and held there for 10 hr while recording the weight as a function of time. The derivative of the weight loss versus time is employed to calculate the evaporation rate. Since the evaporation rate is proportional to the free-surface area of oil in the TGA pan, the evaporation flux in kg/m²-sec is employed to compare additive volatility. This method can also be used to estimate the vapor pressure [65].

Isothermal TGA measurements are carried out on pure tetraester oil, and tetraester oil containing 5 wt % of individual additives to determine their relative volatility at 125°C. A comparison of the relative volatility, in terms of the evaporation flux, is listed in Table 7. The reference evaporation flux of the pure tetraester oil is in the first row. BHT has the highest evaporation flux, and the evaporation flux of PNA, PZ, and ZDTC/mineral oil 50/50 is slightly above that of the pure oil. The evaporation rate of 5 wt % ZDTC alone in tetraester oil, and the remaining additives, are no higher than that of the pure oil.

6.2 Accelerated Degradation Tests

6.2.1 Isothermal Pressure DSC

Isothermal differential scanning calorimetry at an elevated oxygen pressure is widely employed for rapidly evaluating thermal stability of grease [e.g., 66]. This is referred to as the pressure DSC, or PDSC, measurement. PDSC measurements are done on greases to compare the thermal stability of experimental grease formulations. Since dissolved iron is implicated in bearing failure, the effect of dissolved iron on thermal stability is also investigated with the PDSC. In the PDSC test, 5–10 mg of grease are placed in the open DSC pan, the oxygen pressure is increased to 3.4 MPa, and the temperature is rapidly increased and held constant until the combustion exotherm is observed. The time until the combustion exotherm is referred to as the induction time. This procedure is repeated at a number of different temperatures for each

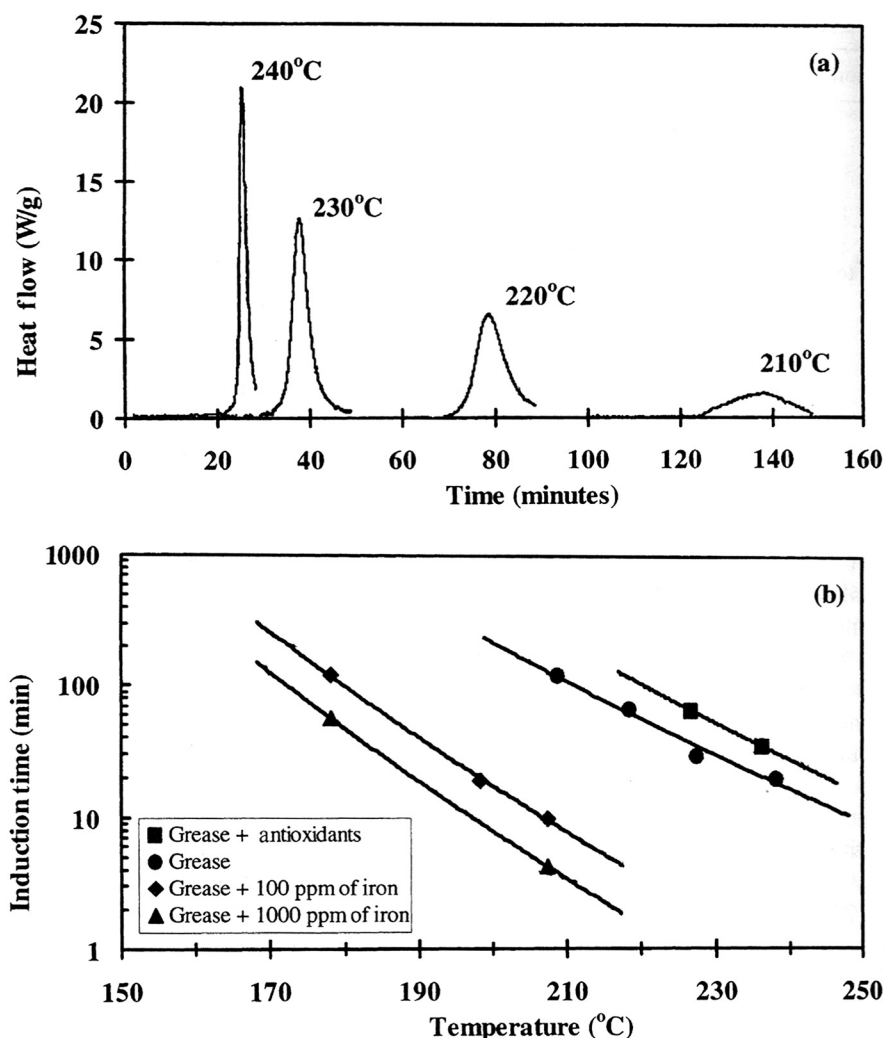


Figure 9 Isothermal pressure DSC exotherms (a), and induction time versus temperature showing the effect of antioxidants and dissolved iron (b) in the commercial lithium grease.

sample. Typical combustion exotherms for the lithium grease without additives are shown in Figure 9a. For comparing additives, the induction time is plotted as a function of temperature. Figure 9b shows how the induction time is increased by antioxidants and decreased by dissolved iron. Addition of DMD to the lithium grease, in combination with antioxidants and ZDTC, significantly improves the induction time in the presence of dissolved iron.

6.2.2 Nonisothermal Pressure DSC

Since oil oxidation leading to bearing failure in the disk drive spindle motor bearings is partly due to metal-catalyzed oxidation of the oil, further optimization of the additive

package is done on oil without the thickener. Although isothermal PDSC measurements are useful on formulated grease, they do not provide reproducible induction times for oil without thickener. A nonisothermal pressure differential scanning calorimetry (NIPDSC) procedure enables testing of additives in oils. For each measurement, 5–10 mg of the oil are placed in the open DSC pan. The oxygen pressure is increased to a constant pressure between 0.55 and 3.4 MPa. The sample is then heated at a constant rate between 1–20°C/min until the occurrence of the combustion exotherm. The exotherm onset temperature and total heat flow do not exhibit any regular dependence on oxygen pressure. An oxygen pressure of 3.4 MPa was selected for consistency with the PDSC measurements.

An example of the NIPDSC test on tetraester oil with and without antioxidants is shown in Figure 10. The exotherm temperature generally increases, and the exotherm becomes sharper, with increased heating rate, as shown in Figure 10. At the higher heating rates, the internal heating upon combustion skews the shape of the exotherm, but it is still possible to determine the onset temperature. Incorporating antioxidants in the oil (Figure 10b) increases the onset temperature of the exotherm as a function of heating rate. The NIPDSC test is useful for rapidly screening the thermal stability of base oils and stabilizing additives.

6.2.3 Bulk Oil Oxidation

Pressure DSC (PDSC and NIPDSC) can be employed to quickly screen a large number of oil, grease, and additive combinations with a relatively short amount of time required for each test on a given sample. However, the onset temperature for the exotherm in the DSC tests is approaching the flash point of the oil, and they are done under pure high-pressure oxygen. At the conditions of the pressure DSC test, the kinetics of oxidation/stabilization may differ from those in air at lower temperatures. It is also not possible to monitor the oxidation chemistry and physical changes associated with oil degradation in the pressure DSC tests because the sample is destroyed during the test. Real bearings contain oil in contact with solid metal surfaces, and this situation cannot easily be reproduced in the small aluminium pan of the DSC test.

Extensive characterization of ester oil degradation at elevated temperature in the presence of metals was performed at the Pennsylvania State University with a micro-oxidation test [29,67–70]. In the micro-oxidation test, it is generally found that the oils have undergone a significant increase in molecular weight due to free-radical polymerization after less than 100 hr at 250°C. In the bulk-oil oxidation tests described below, the only significant oxidation reactions detected are those shown in Figures 5–7. The products formed in these oxidation tests performed at lower temperatures differ from those formed in the micro-oxidation test because of the much higher temperature used in the micro-oxidation test.

A more gradual type of accelerated aging test is performed at lower temperatures, which provides continuous contact of the oil with solid bearing metals and allows for periodic sampling and chemical analysis to follow the oxidation chemistry. With the tetraester oil employed in disk drive spindle motor bearing grease, 4 g of oil are combined with the desired amount of additives in a 150-ml Pyrex beaker (53 mm in diameter) and placed in an oven. The setup is schematically shown in Figure 11a. This arrangement provides an adequate surface area so that the reaction rate is not

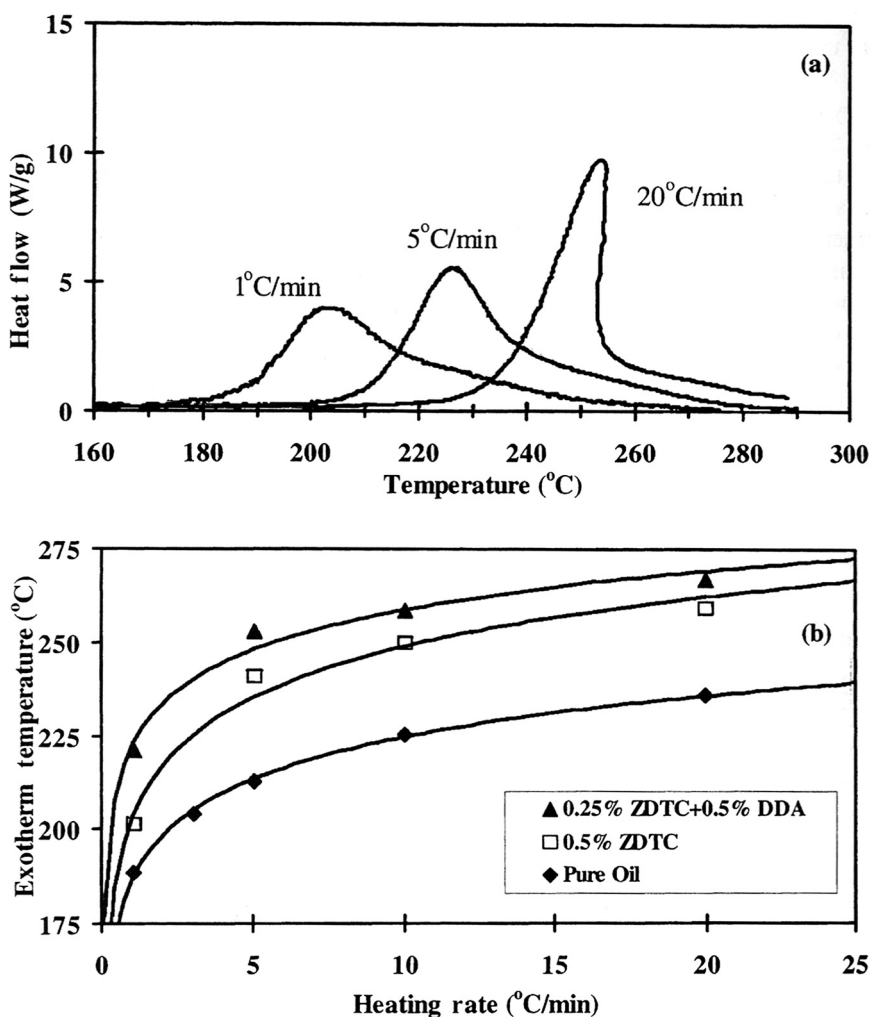


Figure 10 Non isothermal pressure DSC exotherms (a), and the temperature at the onset of the exotherm with two combinations of antioxidants (b), in the tetraester oil.

limited by the rate of oxygen diffusion into the oil. The beakers were lightly covered with aluminum foil and perforated with a 7-mm-diameter hole near the center for drawing oil samples into a pipette. Steel balls are included in most of the tests (3/32 in. in diameter, 304 stainless steel).

Fluid-bearing spindle motor oils must have a lower viscosity than the grease oil, so that the vapor pressure is significantly higher, which requires a modification of the bulk-oil oxidation test setup. For example, at 150°C DOS oil would evaporate before it significantly oxidized. The experimental setup used to evaluate the oxidation stability of the fluid-bearing oils is shown in Figure 11b. For each test, 10g of the formulation were placed in the three-neck flask. A combination of 40 steel balls and 0.25g of leaded bronze powder (metals) were included along with the oil. A magnetic stirrer continuously agitates the metals in the oil. The stirring

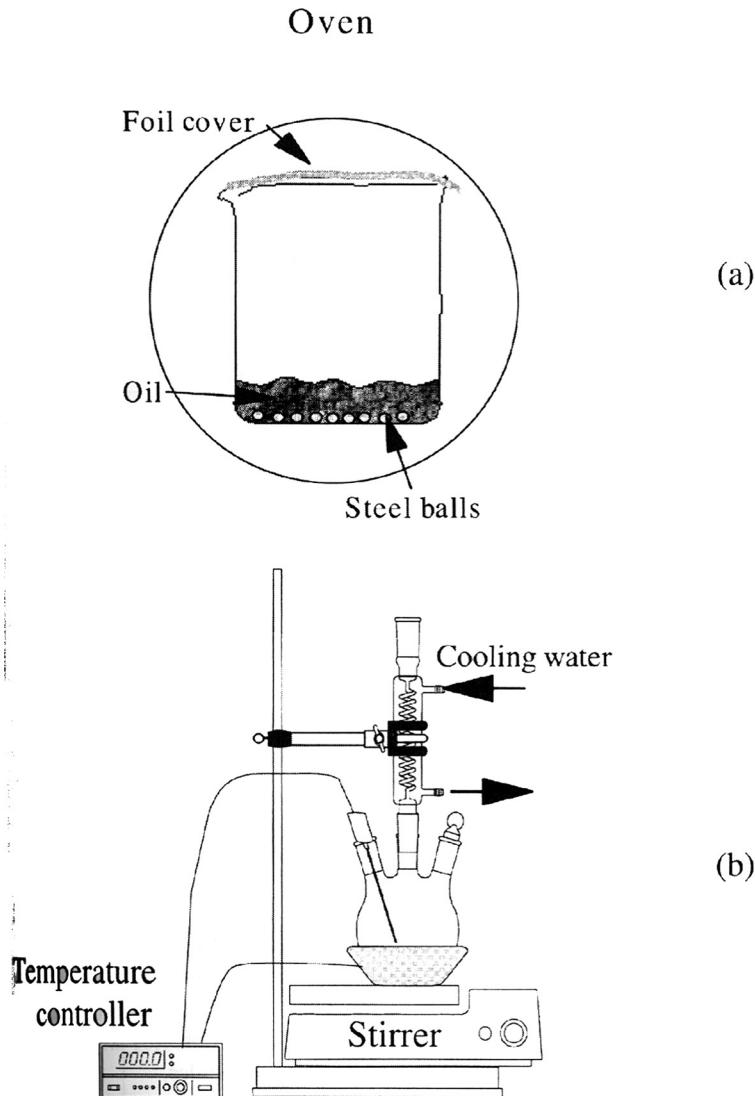


Figure 11 A schematic of the accelerated oil oxidation test setup for aging bulk quantities of oil. Beaker in oven with steel balls for tetraester oil (a) and stirred three-neck flask with condenser and heating mantle for the more volatile fluid-bearing oils (b).

provides abrasion to simulate intermittent contacts in the bearing. The oil temperature is held at $150 \pm 5^\circ\text{C}$ by the temperature controller. The thermocouple is enclosed in a glass thermowell to avoid direct contact with the oil. Oil vapor is retained in the heated flask by the condenser. The open end of the condenser provides exposure of the oil to atmospheric oxygen. Several drops of oil are periodically drawn from the flask through the neck with the glass stopper. The sampling period is between 1 and 5 days.

6.3 Chemical Analysis

The ability to periodically sample the oil enables a broad spectrum of chemical analysis to be employed for characterizing the oxidation and stabilization chemistry.

6.3.1 Differential Scanning Calorimetry

There is not enough sample available to periodically measure viscosity of all the samples being aged with the various additive combinations. However, changes in the viscosity can be inferred from changes in the glass transition temperature through the WLF equation [71]. For example, the viscosity of DOS oil is given by

$$\log(\eta) = 9.779 - 11.47 (T - T_g) / (45.17 + T - T_g) \quad (18.1)$$

where η is the Newtonian viscosity in mPa-sec, T is the viscosity measurement temperature, and T_g is the glass transition temperature of the oil. The WLF coefficients are calculated from capillary viscosity measurements between -20 and 100°C .

The glass transition temperature measured with a modulated differential scanning a calorimeter for several of the model fluid-bearing oils before and after aging with and without bronze powder catalyst are listed in Table 8. The oil viscosity calculated from Eq. (1) and the T_g is also listed in Table 8. Aging increases the viscosity through the increase in T_g .

The T_g increases with aging due to the formation of hydroxyl groups on the hydrocarbon chains [72]. The T_g increases less in the presence of the bronze. In a previous study [24] the presence of dissolved iron increased the formation of hydroxyl groups on the oil chains, which is expected from the catalytic reaction scheme shown in Figure 6. Since the sintered bronze powder has a high surface area, most of the oil chains with one or more hydroxyl groups adsorb onto the surfaces of the powder. Thus the T_g of the oil increases more in the absence of the metal catalyst powder.

6.3.2 Gel Permeation Chromatography

As the oil oxidizes, the molecular weight could also be increased through free-radical polymerization. One way of measuring molecular weight is by gel permeation chromatography, GPC [67]. In GPC a dilute solution of the oil is injected into a solvent stream flowing over a packed column of porous media. The time between the injection and the elution of the oil through the column into a detector at the outlet decreases with increasing molecular weight of nonpolar molecules.

Table 8 Glass Transition Temperatures for Fluid-Bearing Oils Before and After Thermal Aging with and Without Metal Catalyst

Oil	Treatment	Catalyst	Glass transition temperature ($^\circ\text{C}$)	Viscosity at 40°C (mPa-sec)
DOS	Initial oil	—	-106.0	10.2
	Aged	None	-89.8	18.6
		Bronze powder	-99.8	12.9
PAO	Initial oil	—	-111.5	5.3
	Aged	None	-103.2	6.6
		Bronze powder	-106.6	6.0

Note: Aging was for 740 hr at 140°C , 10 g of oil, 0.25 g of bronze powder, no stirring.

Four GPC columns, each 300 mm long, are connected in series. The GPC column packing media is styrene/divinylbenzene copolymer with a pore size of 10microns. The solvent is tetrahydrofuran (THF), and the flow rate is 1 ml/min. Measurements are carried out at 40°C. Calibration is done using 24 monodisperse polystyrene standards with different molecular weights between 500 and 3,000,000 Daltons. Samples are introduced into the GPC columns by injecting 100 microliters of 1 to 2mg/ml of oil dissolved in THF.

The apparent increase in molecular weight during accelerated aging tests on the tetraester oil with antioxidants is shown in Figure 12. For nonpolar molecules, the hydrodynamic volume of diffusing species in the eluent determines the retention time. The average molecular weight of the tetraester oil is 522 Daltons, while the

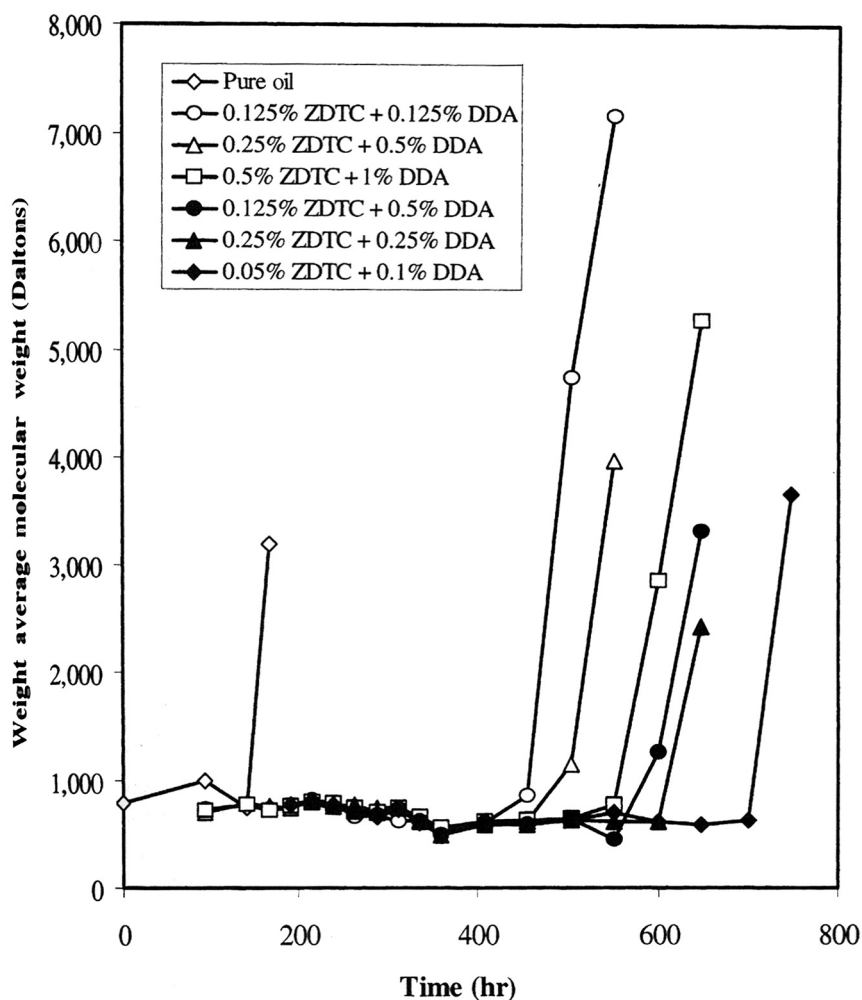


Figure 12 Apparent molecular weight from gel permeation chromatography during accelerated aging of the tetraester oil with different amounts of primary antioxidant DDA and secondary antioxidant ZDTC, with four ball bearings in the oil.

number average molecular weight from GPC gives 787 Daltons for the molecular weight of the initial oil. The difference is attributed to a different relationship between the hydrodynamic volume and molecular weight for the polystyrene versus the tetraester. Intermolecular association through hydrogen bonding increases the hydrodynamic volume of the flow unit. For interpretation of the GPC elution curve, the hydrodynamic volume is assumed to be a function of the molecular weight. However, in the presence of oxidation products, the retention time is determined by the hydrodynamic volume of the associated species [73].

The apparent molecular-weight increase of the oil with aging in Figure 12 actually reflects an increase in the degree of association between oxidized tetraesters [24]. As described in the LDMS Analysis section 6.3.6, chemical dimers (and low-molecular-weight polymers or oligomers) are absent from the LDMS spectrum. The apparent molecular-weight increase up to 3190 and 7167 Daltons probably arises from flow units comprising 6 to 13.7 of the partially oxidized tetraester molecules, respectively.

Figure 12 shows the stabilization of the tetraester oil by various combinations of primary and secondary antioxidants DDA and ZDTC, respectively. One of the goals in developing an antioxidant package to stabilize oil is to obtain the maximum stabilization with the minimum amount of antioxidants. Here the longest lifetime was obtained with the least amount of antioxidants. These effects arise from the complex interaction between the primary and secondary antioxidants, as outlined in Figure 7, and the corrosive effect of sulfur acids produced by decomposition of the secondary antioxidant ZDTC.

6.3.3 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy provides a window into the oxidation chemistry [74]. NMR measurements on hydrocarbon oils are performed in a nuclear magnetic resonance spectrometer equipped with a 250-MHz superconducting magnet. The preferred solvent is chloroform- d_1 (99.8 atom % D, CDCl_3). Oil solutions in chloroform are held in 5-mm-diameter NMR tubes. For proton acquisitions, the spectrometer is set to a spectral width of 5000 Hz, a 45° pulse width of 3 μsec , 2048 scans, and a relaxation delay of 1 sec.

Typical NMR measurement results are shown to illustrate how this technique is employed to follow the consumption of antioxidant and oil oxidation chemistry with the tetraester oil. The region of the NMR spectrum that contains the internal methylene $-\text{CH}_2-$ (1.23 ppm) and end methyl protons $-\text{CH}_3$ (0.87 ppm), as well as the methyl protons on the tertiary butyl end groups of DDA (0.57 ppm), is shown in Figure 13. The definition of internal and end protons is shown in Table 9. The two peaks in between the internal $-\text{CH}_2-$ and the end methyl protons $-\text{CH}_3$ arise from the presence of some chain branching on the original tetraester. The upper dark curve in Figure 13 and the insets is the initial spectrum. The peak area is proportional to the number of protons in the indicated chain segments, or mole fraction of DDA, respectively. The lower light curve in Figure 13 is the spectrum of the tetraester oil with additives after aging. Both before and after aging, the peak area of the pentaerythritol proton $\text{C}(\text{CH}_2 \text{ O})_4$ peak area is used to normalize the NMR spectra, so that the observed decreases in the peak areas shown in Figure 13 reflect the loss of the indicated protons from the oil with aging at 150°C . A full analysis for the NMR spectrum of this oil is in [24].

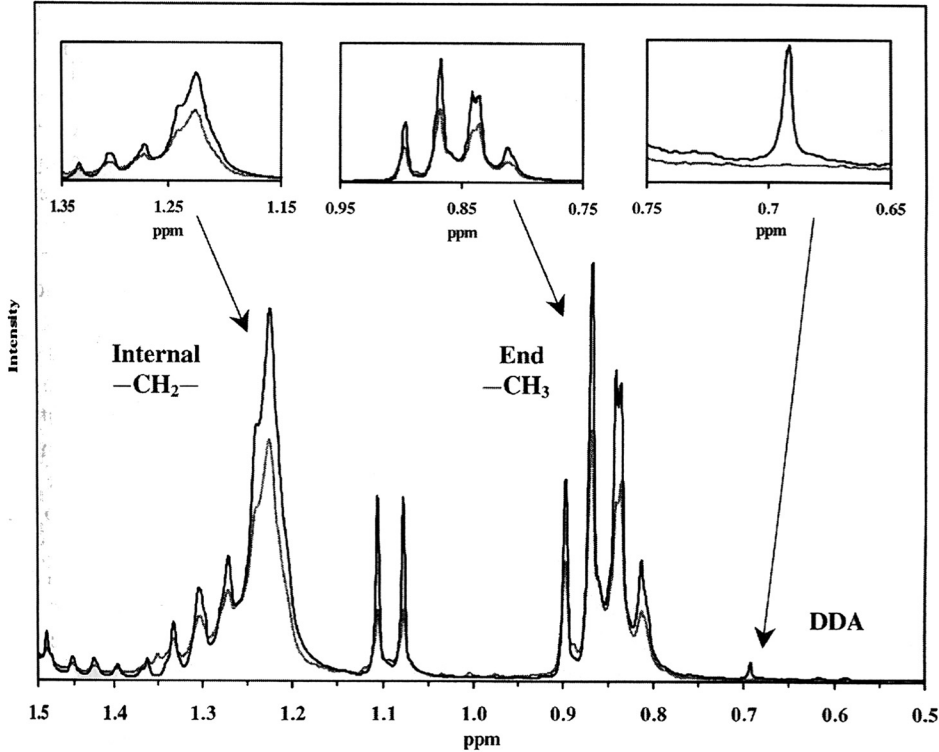


Figure 13 Proton NMR spectrum of tetraester oil before and after aging for 4500 hr at 150°C with no metal catalyst present and 1% equimolar ZDTC/DDA (0.75% DDA, 0.43% ZDTC).

Table 9 Definition of Internal-CH₂- and End-CH₃ Groups in the Tetraester oil

Acid chain	Protons designation
Pentanoic	<div><div>InternalEnd</div><div><div><div><div>O</div><div> </div></div><div><div>O</div><div>—</div><div>C</div><div>—</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH₃</div></div><div><div>↓</div><div>↓</div></div></div></div></div>
Nonanoic	<div><div>InternalEnd</div><div><div><div><div>O</div><div> </div></div><div><div>O</div><div>—</div><div>C</div><div>—</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH₃</div></div><div><div>↓</div><div>↓</div><div>↓</div><div>↓</div><div>↓</div><div>↓</div></div><div><div>↓</div></div></div></div></div>

Small amounts of secondary antioxidant ZDTC cannot be distinguished within the overlapping peaks of the oil. However, the tertiary butyl proton peaks of the primary antioxidant DDA near 0.67 ppm are clearly visible in the upper right inset of Figure 13. The area of the DDA peak can be used to quantitatively measure the DDA concentration in the oil as a function of aging time. For this example, there are 18 tert-butyl protons in the DDA, and 8 pentaerythritol protons in each tetraester oil molecule. Thus, the moles of DDA per mole of oil are (8/18) times the normalized DDA peak area. The DDA concentration in the oil as a function of time for samples containing ball bearings or dissolved iron is shown in Figure 14. There is an induction period, even with dissolved iron. The induction period is probably due to the accumulation of the peroxide intermediate in the chain reaction, Figures 5–7. Oil failure takes place when the DDA concentration reaches zero. Even 5 or 10 ppm of dissolved iron shorten the oil life more than the solid metal; 50ppm of iron shortens the oil life about 20% more than 5 or 10ppm. Without any metal present, the oil lifetime is about 4,500 hr at the same composition and concentration of antioxidants. Medvedeva et al. [75] report a similar decrease in antioxidant concentration during photochemical oxidation and in rolling contact bearings.

NMR spectroscopy also enables tracking the loss of protons on the oil chains. Initially there are $4 \times 3 = 12$ end $-\text{CH}_3$ protons per tetraester, and somewhere between 8 and 40 internal $-\text{CH}_2-$ protons per tetraester. For this oil, there were about 18 internal $-\text{CH}_2-$ protons per tetraester, which implies about a 70:30 mole ratio of pentanoic to nonanoic acid in the reaction mixture used to make the oil. As the oil oxidation reaction proceeds without any antioxidant, both the internal and end protons gradually decrease with time, as shown in Figure 15a. The loss of end methyl groups is due to the chain cleavage reaction, and the loss of internal methylene protons is due to a combination of chain cleavage and hydroxyl group formation (Figure 5). Oxidation is inhibited by the stabilizing antioxidants, also shown in Figure 15a. The NMR peak areas for the stabilized oil in Figure 15a show a gradual increase in the number of internal methylene groups $-\text{CH}_2-$ with little increase in the end groups, $-\text{CH}_3$. This is consistent with evaporation of the lower-molecular-weight tetraesters, leaving behind the higher-molecular-weight moieties with a higher number of internal methylene protons per chain. When the anti-oxidant has depleted, there is a sudden, nearly explosive conversion of the oil to oxidation products.

6.3.4 UV/Visible Spectroscopy

A view of the oxidation chemistry through NMR spectroscopy is augmented by UV/visible spectroscopy, which is sensitive to the bond absorption of the antioxidants and some of the oxidation products [24,67]. The UV absorbance spectra are measured with a diode array spectrophotometer. For the UV measurements, one drop of oil is placed between two quartz disks (quartz wafer 25-mm diameter, 0.5-mm thick) and held in the beam during the wavelength scan. The absorbance reference is the pure oil before any aging. The UV/visible absorbance spectrum is measured between 100 and 500 nm.

A typical plot of the UV/visible absorbance spectrum measured during the same accelerated aging test shown in Figures 13 and 15 is shown in Figure 16. The ZDTC has absorption peaks at 212 and 266 nm, and the DDA has absorption

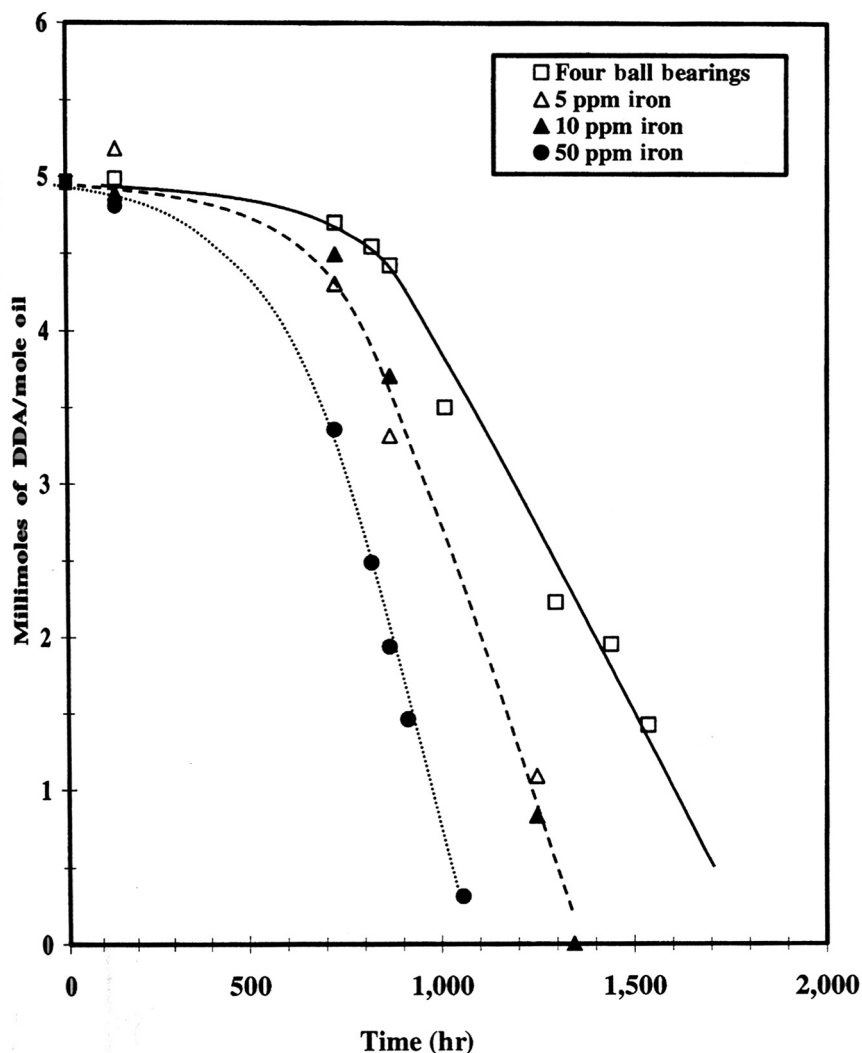


Figure 14 Mole fraction of primary antioxidant in tetraester oil during accelerated aging at 150°C, in the presence of ball bearings or with various amounts of dissolved iron. The initial antioxidant concentration was 0.5 wt% DDA and 0.5 wt% ZDTC.

peaks at 210 and 290 nm. There is some evidence for a ZDTC/DDA complex formation, because the absorption spectrum of the binary solution of the two antioxidants in the tetraester does not match a linear combination of the spectra from the individual antioxidants in the oil. Inoue and Watanabe [76] further discuss interaction between oil additives.

As the oil initially containing an equimolar solution of the two antioxidants ages, the absorption peak in the neighborhood of 266–290 nm gradually disappears, corresponding to the loss of DDA observed by NMR spectroscopy. Other absorption peaks between 200 and 300 nm are due to the formation of ketone

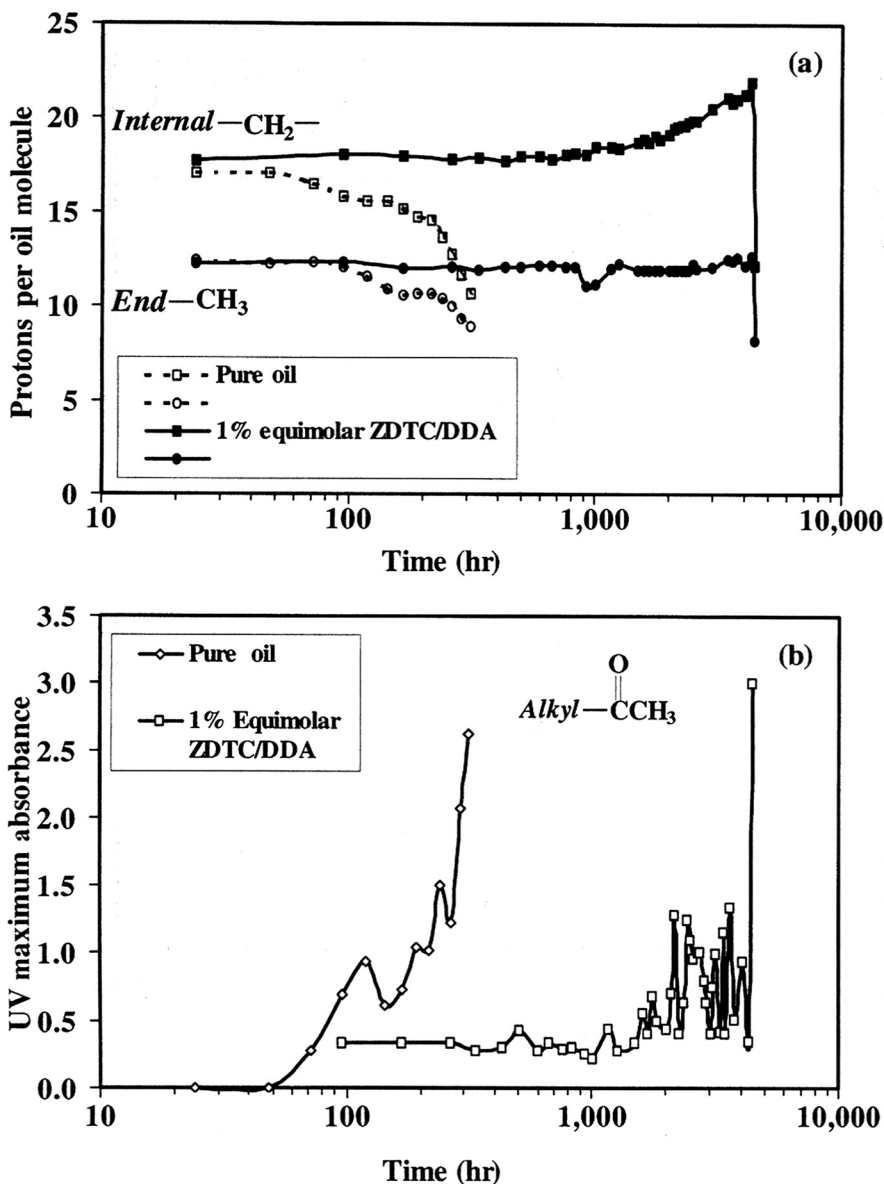


Figure 15 Average number of internal methylene and end methyl protons per molecule from NMR (a), and UV absorbance maximum during the accelerated aging test on pure oil and oil with antioxidants (b). Aging was at 150°C with no metal catalyst present and 1% equimolar ZDTC/DDA (0.57% DDA, 0.43% ZDTC).

oxidation products. The maximum absorbance during aging of pure oil, and the 1% equimolar ZDTC/DDA, are plotted in Figure 15b. As with the NMR, this also shows the nearly explosive conversion of the oil into oxidation products following a long induction period.

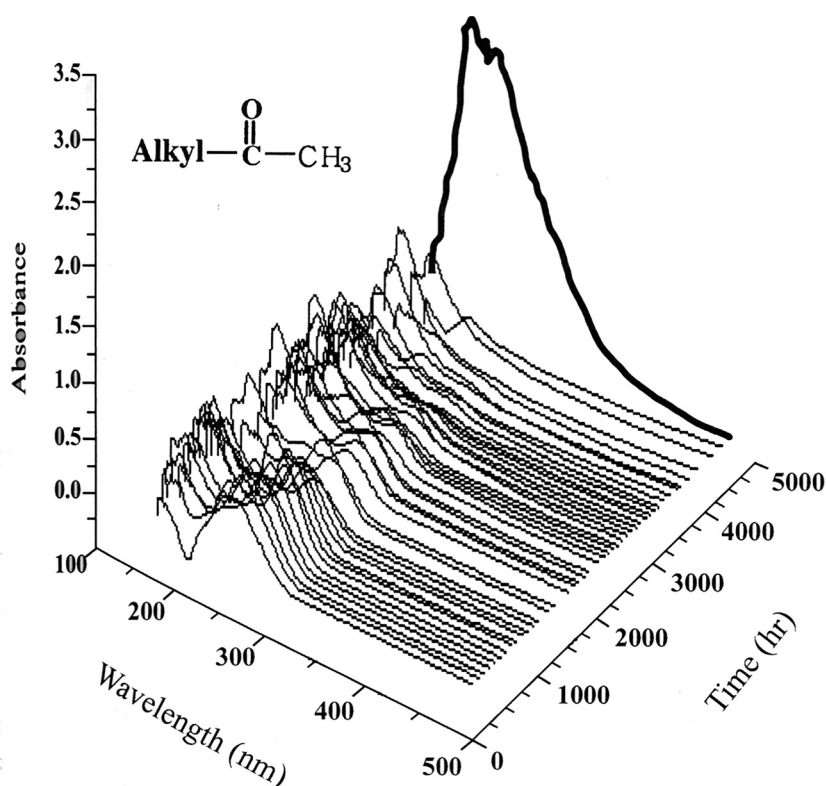


Figure 16 Three-dimensional plot showing the UV/visible absorbance spectra during the accelerated aging test on tetraester oil. Aging was at 150°C with no metal catalyst present and 1% equimolar ZDTC/DDA (0.57% DDA, 0.43% ZDTC).

6.3.5 Thin-Layer Chromatography

Thin-layer chromatography (TLC) provides valuable insight into oxidation chemistry [77,78]. This technique is useful on formulated greases, as well as oil, throughout the progress of oxidation. For this technique, a very small amount of the oil to be tested is dissolved in a solvent, a spot of the solution placed on a glass plate coated with silica gel, and dried, leaving behind the oil on the silica gel. The lower part of the plate is then placed in a pool of solvent in the bottom of a sealed developing jar. The solvent migrates up along the silica gel, carrying the oil components along at different rates. For oil analysis, the solvent composition is fine-tuned to separate the oil from the additives and oxidation products. Thus, the TLC method can be used to follow antioxidant depletion and oil oxidation in samples drawn periodically during accelerated aging tests.

TLC measures the mobility of the oil in a solvent flow migrating along the surface of a 1 × 3-in. glass plate coated with 250 mm of silica gel (60 Å). The oil is deposited in a spot near one short edge of the plate as ≈ 5 microliters of 5 wt % oil solution in ethyl acetate. The ethyl acetate is allowed to dry, and the TLC plate

is exposed in a TLC chamber for about 1 hr in mixed solvent *n*-heptane/ethyl ether 6/1 v/v as in [24,77]. After exposure, the plate is removed from the TLC chamber, allowed to dry, and developed with iodine vapor in a sealed container at room temperature to observe how far the oil fractions migrated along the silica gel. Increasing polarity decreases the migration rate of oil relative to the solvent front, because the more polar species have a higher affinity for the silica gel.

A developed and exposed TLC plate with the initial tetraester oil sample, oil aged for 144hr, and oil aged for 168hr is shown by the three streaks in [Figure 17a](#). The oil migrates vertically along the silica gel layer from the initial spot at time zero. The intensity of the streak is proportional to the areal density of oil on the plate at a given location. Each oil sample consists of at least two fractions having different polarity. The polarity increases with increasing oil oxidation. The initial oil consists of two fractions, with the minor one more polar than the major one. The aged oil consists of three fractions with different degrees of polarity. A significant fraction of the aged oil is so polar that it remains in its original location, as indicated by the dark circular regions at the lower end of the plates in [Figure 17a\(2\)](#), [a\(3\)](#), and [b\(3\)](#).

TLC is particularly useful for detecting the presence of additives obscured in the NMR and UV/visible measurements. The TLC chromatogram of the tetraester oil formulated with DDA and ZDTC is shown in [Figure 17b\(1\)](#). The oil, DDA, and ZDTC are clearly separated from one another. The DDA and ZDTC gradually disappear with aging. [Figure 17b\(2\)](#) shows the oil just prior to failure. The antioxidants are gone, and the oil mobility is relatively unchanged. While aging for only one more day, the oil suddenly oxidized, as determined from NMR and UV/visible spectroscopy as described above, and the TLC mobility decreased; see [Figure 17b\(3\)](#). The decrease in the mobility reflects the formation of polar hydroxyl and carboxylic acid oxidation products on the oil chains.

6.3.6 Laser Desorption Mass Spectrometry

A highly sophisticated and powerful technique, which has the potential for revealing the details of the oxidation/stabilization chemistry, is laser desorption mass spectrometry (LDMS). For a complex oil/additive system undergoing oxidation, the techniques described above are not unambiguous in their interpretation. The use of multiple techniques helps to clarify the interpretation, but identification of specific products and intermediates is often impossible, especially for very small samples. The atomic mass of products and intermediates greatly assists in narrowing the possibilities. Standard mass spectrometry and secondary ion mass spectrometry measures the masses of ionized fragments of species present in the oil. The fragmentation process renders a complex spectrum with its own set of unknowns.

Parent ion molecular mass spectra were obtained with an LDMS developed in our laboratory. The apparatus employs vacuum UV (125nm, 10eV) photoionization mass spectrometry with jet cooling to avoid fragmentation of the organic molecules. The apparatus is fully described in [79]. Approximately 1–5 mg of the oil are deposited onto a pyrolytic graphite plate for the measurement. The LDMS spectra provide the only existing means to directly observe the mass distribution in a mixture of intermediate molecular-weight organic compounds. An LDMS spectrum of the tetraester oil containing 0.5% ZDTC and 0.5% DDA is shown in [Figure 18a](#).

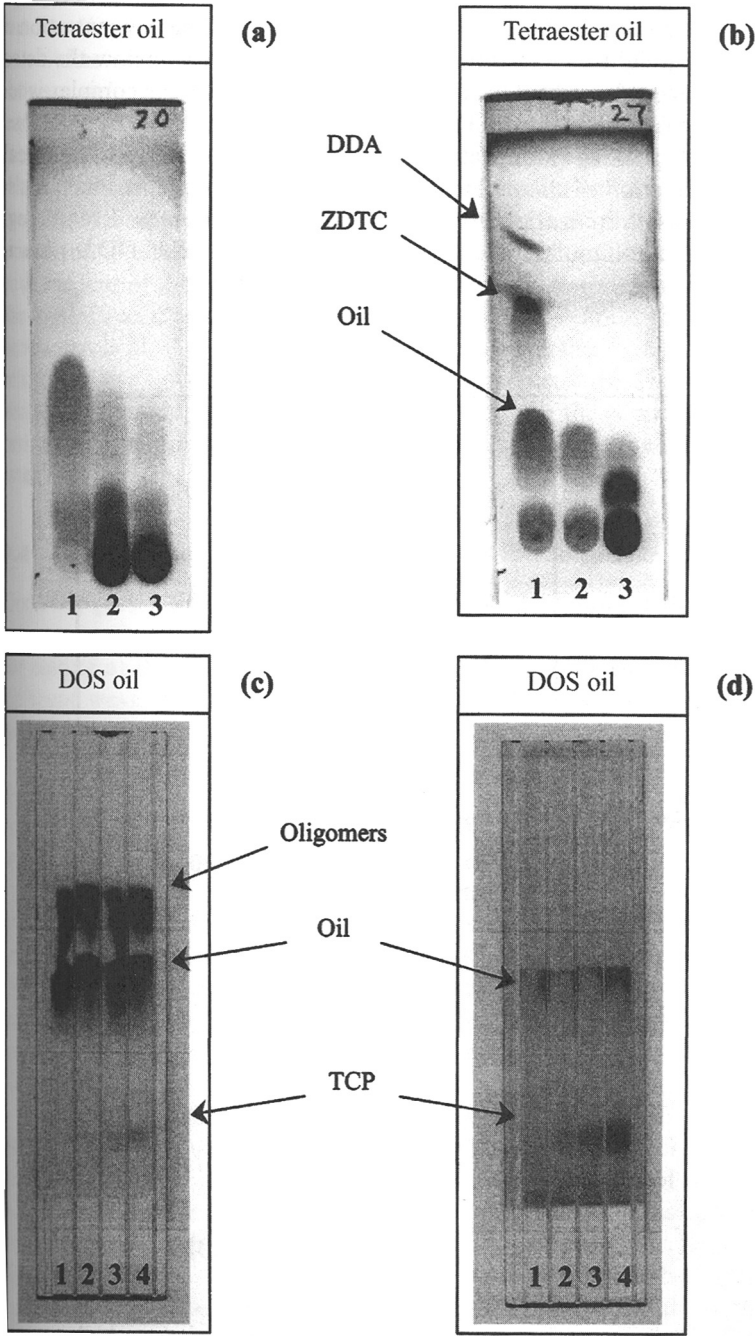


Figure 17 Tetraester oil aged at 150°C with four ball bearings (a) and (b). Pure oil, (1) before aging, (2) aged 144hr, and (3) aged 168hr (a). Oil with 0.25% ZDTC + 0.25% DDA, (1) before aging, (2) aged 600 hr, and (3) aged 648 hr (b). DOS oil with 1% oligomers (c) and (d). (1) no TCP, (2) 0.5% TCP, (3) 1% TCP, and (4) 2% TCP, before aging (a) and after aging for 120 hr at 150°C in the presence of catalytic metals (b).

The individual molecular weights of the individual tetraester molecules from Figure 4 are detected as the sharp peaks at 472, 528, 584, and 641 amu. The concentration of the highest-molecular-weight pentaerythritol tetranonanoate was below the detection limit. The ZDTC could not be detected, presumably because this complex is too unstable and is highly fragmented even by the relatively low-energy process of laser desorption. The DDA peak shows up at 393 amu in Figure 18a. The LDMS peak height is not only a function of the molar concentration of oil constituents but also their capture cross section, ionization efficiency, and UV absorbance. Even though there are only about 5 millimoles of DDA per mole of oil, the DDA peak in

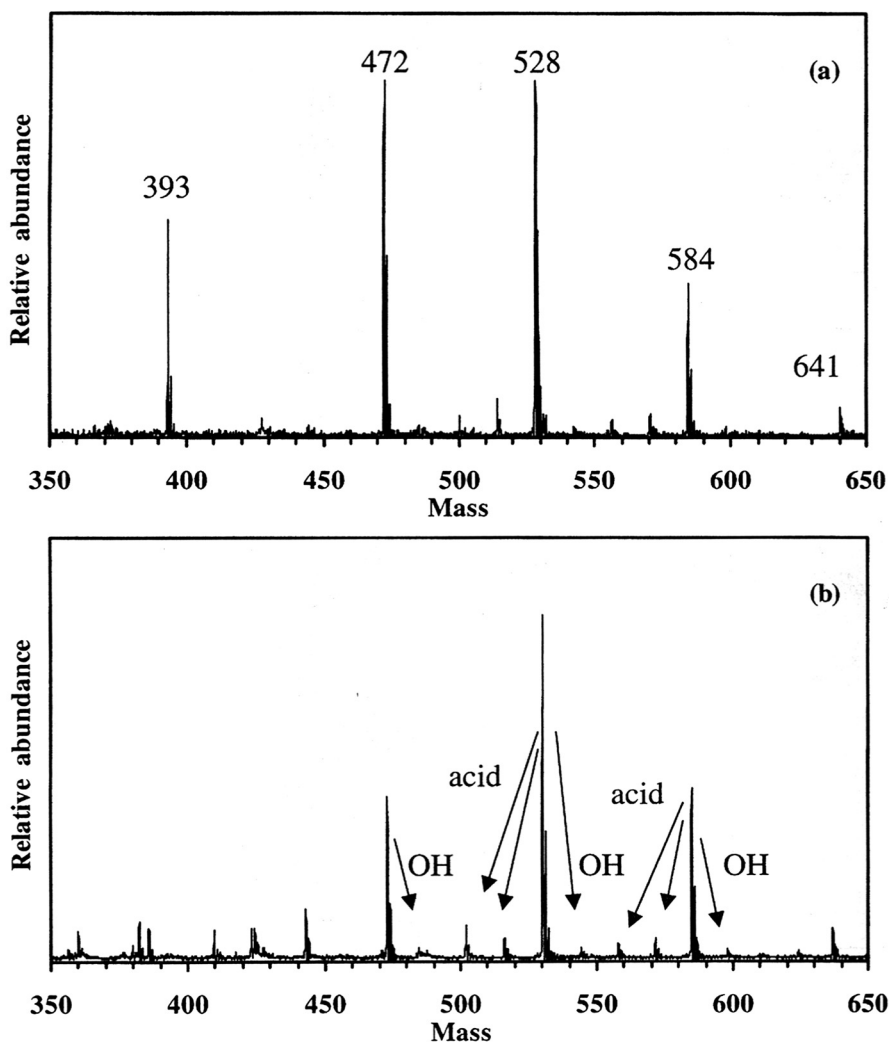


Figure 18 LDMS spectrum of tetraester oil before (a) and after aging for 1440hr at 150°C (b). The oil contained 0.5% ZDTC, 0.5% DDA, and 10ppm of dissolved iron.

Figure 18a is comparable to the oil peak height. Thus, the LDMS is highly effective for detecting trace amounts of certain antioxidants in oil or grease.

After aging for 1440 hr with 10ppm of dissolved iron, the LDMS spectrum shows a rich variety of oxidation products. Most of the mass peaks are associated with their products and mechanism of formation in [24]. In summary, the oil chains increase in mass due to hydroxyl group formation and decrease in mass through chain cleavage (Figure 5). Each hydroxyl group formed on a chain adds 16 amu to the mass. Chain cleavage results in the following products. Formation of carboxylic acid on an attached chain and acetone reduces the mass by 12 amu—and by 26 amu with the loss of 2-butanone. Formation of methyl ketone on an attached chain with the loss of acetic acid reduces the mass by 14 amu—and by 26 amu with the loss of propanoic acid. A pungent odor emanating from the oxidizing oil signals the presence of these low-molecular-weight acids and ketones. The pentanoate should be particularly stable with respect to cleavage because the cleavage mechanism involves proton abstraction from carbons at each end of a three-carbon segment of the alkyl ester chain.

6.4 Ball Bearing Life Tests

Once the grease oil additives package has been optimized through the accelerated aging tests, it is necessary to formulate the additives into a small batch of grease for testing at the bearing and motor level. The additives were incorporated in two different ways: with a co-solvent into finished grease; and at the hot-oil stage of processing. Both methods are described below.

With the lithium grease, it is possible to incorporate an additive solution into the grease with a volatile co-solvent. For example, 20g of grease and the additives are placed in a 120-ml glass bottle, along with 40g of diethyl ether. This slurry of lithium soap suspended in an ether solution of oil and additives is mechanically agitated for several hours on a roller table. The diethyl ether solvent is evaporated at ambient temperature in a rotary evaporator (initially at 84kPa and decreasing to 16kPa over several hours' time) while carefully agitating the mixture and modulating the vacuum to prevent violent boiling. The mixture is then subjected to a higher vacuum (33Pa) at ambient temperature for two days, with the grease mechanically stirred and mixed several times. Finally the grease is held at 70°C for 8 hr at 33 Pa.

Grease with additives is also prepared directly from the hot melt. Small samples of grease are made from lithium 12-hydroxy stearate thickener and the tetraester oil, in a specially designed lab-scale grease mill. First, 45g of oil are combined with 5g of lithium hydroxystearate in a 250-ml Pyrex beaker. This mixture is placed in a beaker fitted with heating mantle, along with a stirring bar, on a magnetic stirrer. The mixture of oil and stearate is heated to 280°C while being vigorously stirred to dissolve the stearate until a clear solution is obtained (for about 60 min). Additives are then dissolved into the hot-oil solution. Immediately following dissolution of the additives, the whole solution is quench-cooled by pouring it onto a glass plate sitting on a slab of dry ice. Upon cooling, the grease is in the form of waxy slabs.

The grease mill comprises two 32-mm-diameter disks perforated with 35 circular holes, each 460 microns in diameter, inside a stainless steel tube. The perforated disks are separated by a 3.8-mm-wide cavity. Grease is forced back and forth through

the holes in the perforated disks by the reciprocating action of two opposing pneumatic cylinders driving Teflon pistons against the perforated plate within the steel tube. Air pressure is alternately applied to the cylinders using a cam and follower arrangement driven by a variable-speed gear motor. The quench-cooled grease was milled for 2 hr at 4 cycles/min and 200 kPa maximum air pressure. This provides a smooth grease with the same yield stress properties as the commercial lithium grease.

6.4.1 Detached Bearing

Accelerated life tests were done to evaluate the commercial lithium grease in typical 5×13 -mm disk drive spindle motor bearings charged with 12mg of grease. The tests were done with an Anderometer under a 19.6 Newton preload at 10,000rpm. The medium Anderometer noise frequency band was periodically recorded at intervals of time during the test at 70 and 90°C. The test results are shown in Figure 3. On the basis of these bearing tests, it was determined that stabilizing additives were needed in the grease.

6.4.2 Motor Level

Once the stabilizing additive system had been developed as described above, accelerated motor life tests were carried out using server-class disk drive spindle motors. At least 20 motors were built using grease with and without additives. The acoustic pressure was measured periodically for each of the motors. Typical acoustic pressure measurements on individual motors containing grease with and without additives are shown in Figure 19a. Average acoustic pressure as a function of time for each of the greases is shown in Figure 19b. The grease with additives performed substantially better in the accelerated motor life tests [80,81].

6.5 Fluid-Bearing Oil

As mentioned, aging tests on the lower-viscosity, more volatile, fluid-bearing oil are run in a three-neck flask with a condenser to maintain the oil in the vessel at 150°C while also providing fresh air at the surface of the oil. The same general techniques of chemical analysis used with the tetraester oil are employed periodically for measurements during aging of DOS and DOA model fluid-bearing oils. There is a distinct difference between the oxidized residue during aging of the fluid-bearing oil and that of the tetraester grease oil. UV/visible spectroscopy exhibited no regular change during oil oxidation. The differences between the tetraester oil oxidation and the diester oil oxidation residue are attributed to loss of volatile low-molecular-weight acids and ketones through the condenser, and adsorption of polar oxidation products on the high surface area of the metal catalyst powder. In addition to being thermally stable, the fluid-bearing oil must be electrically conductive.

6.5.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

Several drops of oil are periodically drawn from the flask through the neck with the glass stopper. The sampling period is between 1 and 5 days. Each oil sample is dissolved in deuterated chloroform, and the proton NMR spectrum is measured. Eventually, the NMR peaks broaden significantly between one sampling period and the next, as shown in Figure 20b and c, compared to the NMR spectrum of the initial

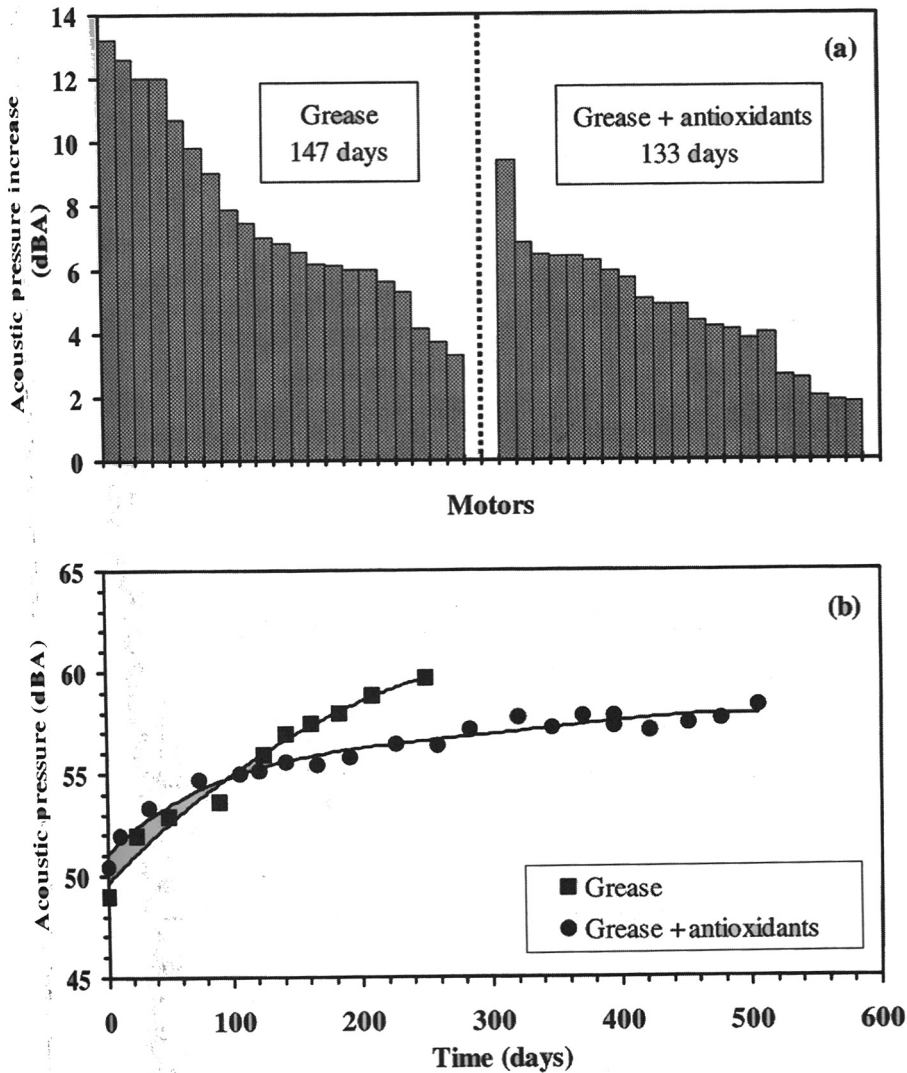


Figure 19 Accelerated motor life test results comparing the commercial lithium grease to lithium grease with stabilizing additives. Acoustic pressure increase measured for individual motors (a), and average acoustic pressure as a function of time (b). The tests were run at 100°C and rotation rate was 10,000 rpm.

oil in [Figure 20a](#). The “lifetime” of the oil formulation is defined by the NMR peak broadening.

The NMR peak broadening arises from the decreased solubility of the polar hydroxyl oxidation products in the chloroform NMR solvent. As the oxidation proceeds, the oxidation products reach their solubility limit and nucleate as micelles. The NMR peaks broaden because the spin-lattice relaxation time is longer for protons on the oil molecules in micelles than it is for protons on oil molecules solution.

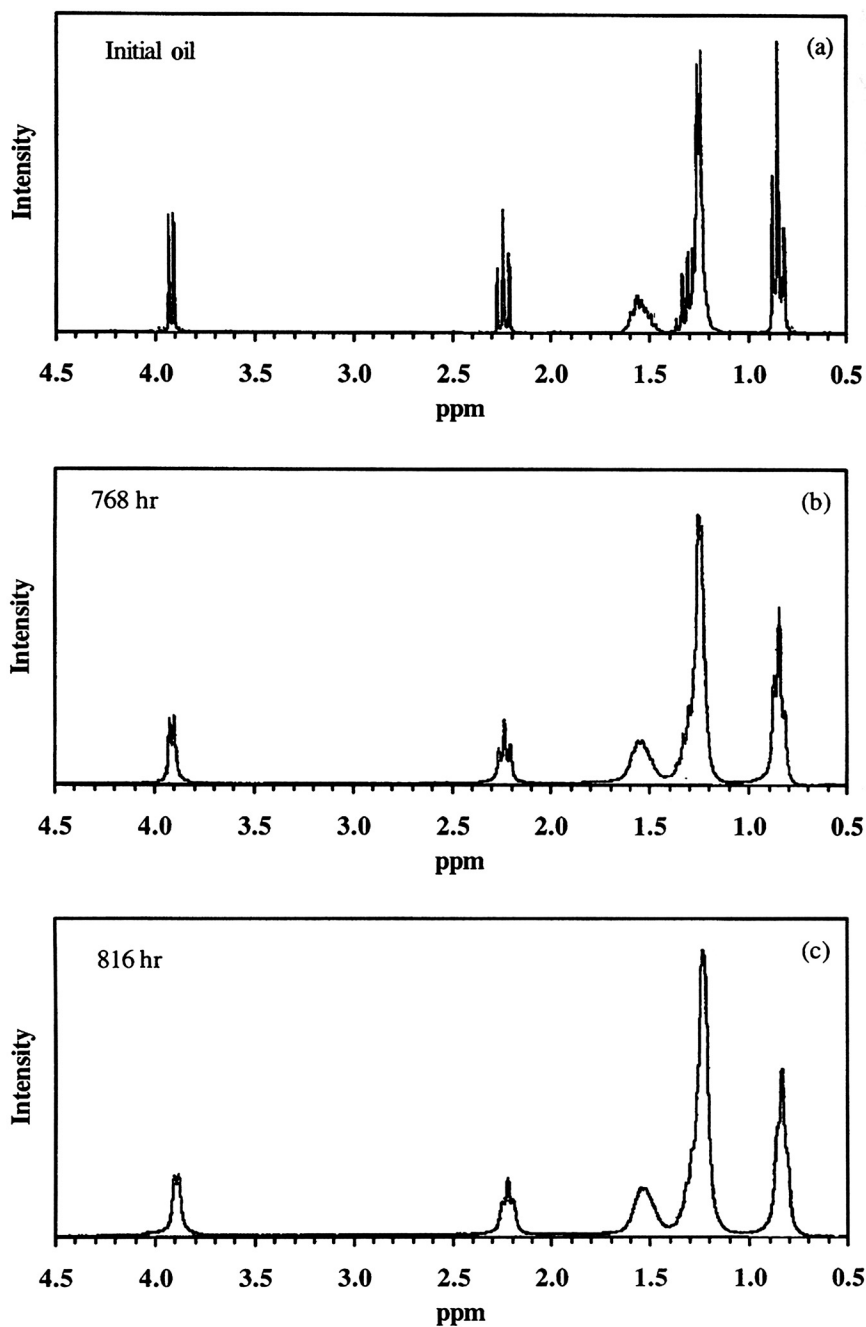


Figure 20 Proton NMR spectra of model fluid-bearing oil DOS during the accelerated aging test. Initial oil (a), after 768 hr (b) and after 816 hr (c) at 150°C , showing the peak broadening that signaled oil failure between 768 and 816 hr. The oil contained 1% ZDTC, 1% TCP, and 0.1 % of the mixed-polymers conductivity additive.

6.5.2 Thin-Layer Chromatography

Antioxidant depletion and the formation of a more polar fraction in the oil during accelerated aging are also observed by TLC. To improve the separation, linear-K, preadsorbent, 5×20 -cm TLC plates with 6-nm silica gel are used with the fluid-bearing oils. Each plate has four separate channels. The initial TLC chromatogram of a formulated model fluid-bearing oils containing 1 % oligomers, and increasing amounts of TCP, are shown in Figure 17c. The oil and additive constituents are clearly separated from one another. Based on the TLC measurements, the oligomeric antioxidants are mostly depleted from the oil within 48 hr of aging. After 120 hr of aging, the oligomer antioxidant is completely depleted, but the metal passivator TCP is still clearly visible in the oil; see the lower streak in Figure 17d (2–4). The point at which the antioxidant is gone from the TLC trade greatly precedes the NMR peak broadening. For the formulations shown in Figure 17c and d, the NMR peak broadening occurs between 552 and 624 hr without TCP, and between 840 and 984 hr with TCP, over this range of TCP concentration. Incorporating 0.1% of the mixed-polymers, conductivity additive decreases the lifetime of the oligomer/TCP formulations by 10 to 20%. DOS oil with 1% oligomers and 1% TCP lasts more than 2000 hr in the presence of ball bearings alone, and only about 780 hr in the presence of catalytic bronze powder (10 g oil and 0.25 g of bronze powder). The greatest detractor from the lifetime of the formulated DOS oil is the catalytic bronze powder.

6.5.3 Viscosity

The oil viscosity measured before and after accelerated aging by capillary viscometry increased by up to a factor of 2 at failure.

6.5.4 Concentration Effects

One of the challenges in determining the optimum formulation is to optimize the concentration of a multicomponent additive system. A metal passivator, such as TCP, controls metal dissolution. The oil lifetime as a function of TCP concentration is shown in Figure 21. There is an optimum amount of metal passivator. Increasing the amount of metal passivator from a very low concentration to the optimum increases the oil stability. Further increasing the metal passivator concentration decreases the oil stability. The existence of an optimum concentration is explained in terms of the oil and additive solubility parameters. The solubility parameter $\delta = \sqrt{E_{\text{vap}}/V}$, where E_{vap} is the vaporization energy and V is the molar volume of oil or additive [82]. The solubility of an additive in an oil decreases with increasing difference between their solubility parameters. Consequently, for a given additive concentration, below the solubility limit, increasing $|\delta_{\text{TCP}} - \delta_{\text{oil}}|$ decreases the solubility of the additive in the oil, hence increasing the surface excess of the metal-passivating additive on the catalytic metal surfaces. Further increasing the TCP concentration above the optimum increases the acidity of the formulation, thus outweighing the beneficial effects of metal surface passivation. The solubility parameter differences and optimum concentrations for the model fluid-bearing oils are listed in Table 10. Similarly, the optimum TCP concentration is also found to result in minimum wear [83,84].

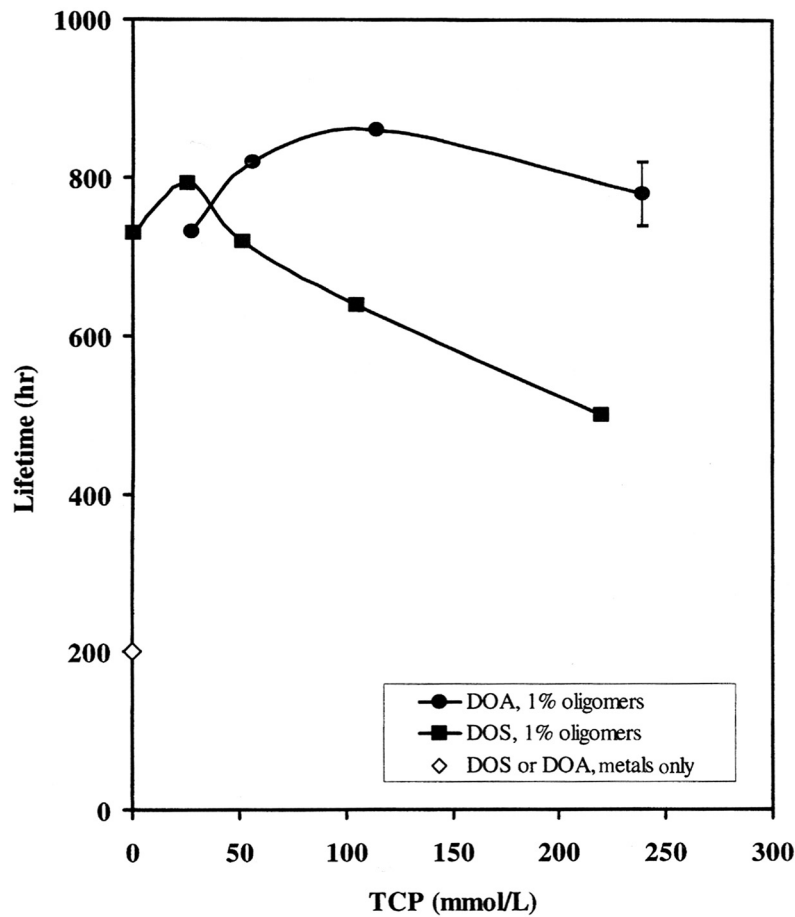


Figure 21 Model fluid-bearing oil lifetime showing the effect of oil type on the optimum TCP concentration.

6.5.5 Conductivity

The conductivity of the fluid-bearing motor oil is measured with a dielectric analyzer. Several milligrams of oil are placed on a ceramic plate patterned with interdigitated gold electrodes. A small-amplitude sinusoidal electrical potential is applied across the electrodes over a range of frequency between 1 Hz and 10 kHz while recording

Table 10 Solubility Parameters, Solubility Parameter Differences, and Optimum Concentration C_{\max} with 1% Oligomers in Model Fluid-bearing Oils.

Oil	δ_{oil} (MPa) ^{1/2}	$ (\delta_{TCP} - \delta_{Oil}) $ (MPa) ^{1/2}	C_{\max} (mmol/L)
DOS	15.2	1.1	25
DOA	15.8	0.5	114

Note: The solubility parameter for TCP is $\delta_{TCP} = 16.3(\text{MPa})^{1/2}$ in MKS units. (Source: Ref. 83.)

the dielectric permittivity and permeability. The oil conductivity is calculated from the low-frequency permeability.

Conductivity as a function of temperature for the two different types of conductivity additives is shown in Figure 22a. The conductivity of the mixed polymers increases with temperature because the charge is transported through the oil by ionic mobility. The conductivity of the PAN is nearly independent of temperature because the conductivity of conducting polymers is metallic-like and decreases with increasing temperature due to lattice vibrations. Charge transport between the conducting polymer probably takes place when PAN molecules collide with one another, and the collision frequency increases with increasing temperature.

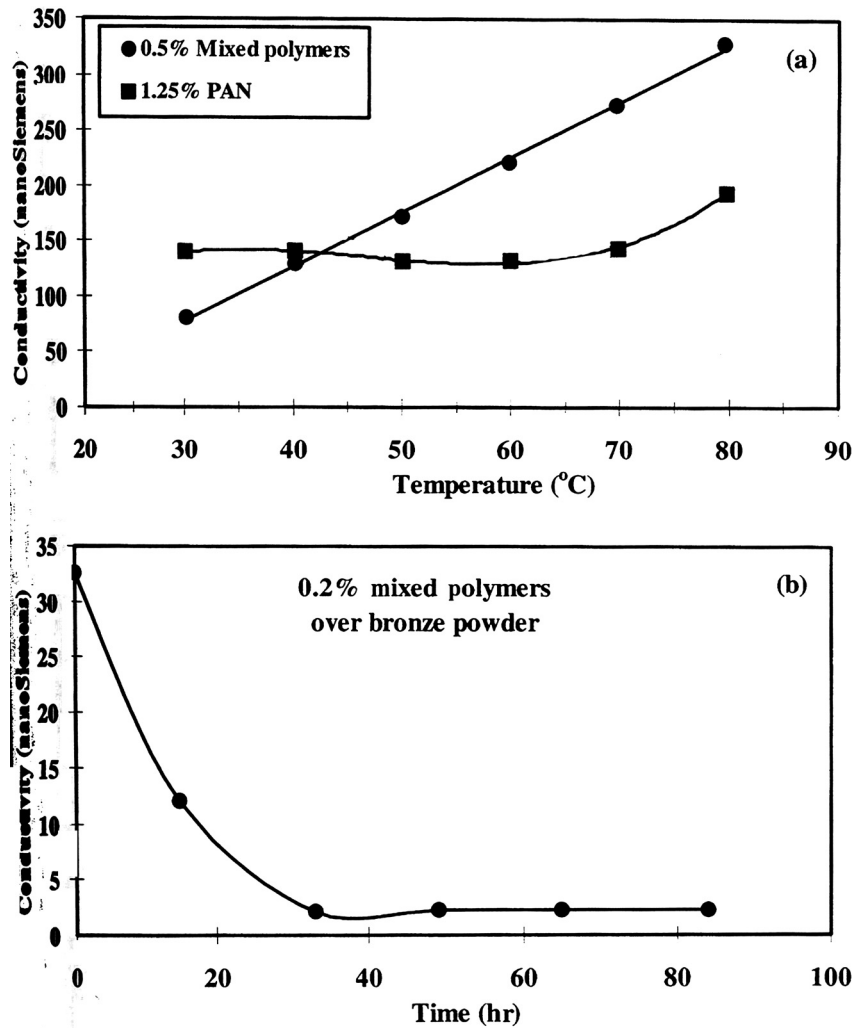


Figure 22 Conductivity of model fluid-bearing oil PAO including polyaniline (PAN) and mixed polymers as a function of temperature (a), and conductivity loss when the formulated oil with mixed polymers is exposed to bronze powder at 50°C (b).

There is a possibility of forming small amounts of powdered bronze wear debris during start/stop operations of the fluid-bearing motor. The effect of bronze powder on the conductivity of PAO oil containing the mixed polymers, conductivity additive is shown in [Figure 22b](#). The conductivity loss in the presence of the bronze powder is due to adsorption of the mixed polymers onto the high surface area of the powder. PAN may be less prone to adsorption than the mixed polymers.

6.6 Disk Lubricant

The subject of disk lubricant additives encompasses an entirely different set of tests and criteria for accelerated life testing. Starting and stopping repeatedly on the disk while recording the maximum frictional force and acoustic emission at start-up has been the most widely used accelerated life test for magnetic recording disk lubricants [23]. Other types of test are the drag test [85] and a low-velocity test [86]. These are combined with visual observation and chemical analysis of the slider and disk test tracks to determine physical and chemical changes that have taken place on the surfaces.

6.6.1 Accelerated Degradation Tests

Many of the factors known to influence the durability of magnetic recording surfaces have been investigated throughout the past two decades; a few are mentioned below. The lubricated overcoat tribology is a function of relative humidity (RH) and test atmosphere [87,88]. Water adsorption on the overcoat is influenced by the lubricant thickness and the orientation of polar end groups [89,90]. Vapors emanating from drive components deposit tribofilms at the slider disk interface [91]. Slider geometry and laser texture together play a role in start/stop durability and environmental sensitivity. The slider disk asperity contacts determine the severity of tribo-interactions between the slider and the disk overcoat [92]. There is a balance among the effects of lubricant thickness, surface roughness, static friction, and durability [93,94]. When the lubricant is depleted, the overcoat undergoes abrasive [95] or tribochemical [96] wear.

The friction coefficient increases with start/stop cycles because the surface energy (hence the work of adhesion) increases sharply as the lubricant film thickness decreases below 0.5 nm [97]. The friction coefficient increases throughout start/stop tests because the lubricant film thickness decreases with time due to removal by asperity contacts in each cycle.

6.6.2 Additive Effects

As mentioned in the section on degradation mechanisms, the perfluoropolyether lubricant degrades by thermal-/mechanical-induced chain scission, which is accelerated by the presence of Lewis acid catalysts such as alumina. Little or no alumina is present in the slider disk interfaces, because both the slider and disk are overcoated with carbon for wear and corrosion protection. Therefore, the primary effect of any perfluoropolyether disk lubricant additive is physical rather than chemical. One drawback of X1-P is its lack of solubility in Zdol, leading to segregation and phase separation in thin films. X1-P preferentially physisorbs on the slider and disk carbon overcoats, eliminating the chemical bonding of Zdol end groups and mitigating dispersion force interaction between the lubricant polymer chains and the overcoat. These effects enhance the Zdol mobility and shorten the chain relaxation times,

thus greatly improving the durability as measured by drag and start/stop accelerated testing [57,85]. An X1-P modified with fluorinated substituents, X-100. Table 6, has improved solubility in Zdol disk lubricant and provides the same improvement in start/stop performance as X1-P [98].

While it is desirable to have good start/stop performance, lower flying heights incorporated in the design of disk drive products in the near future impose new requirements on the interface, even in the absence of physical contacts. As the slider flies over the lubricated disk surface, lubricant moguls form on the disk [99], and lubricant accumulates on the slider [100]. When the slider is laden with droplets of lubricant, transient lubricant meniscus bridges form between the disk and slider. Fracture of the meniscus bridges induces transient adhesion forces that interfere with smooth flying of the slider [101]. Higher-surface-energy hydrocarbon lubricants, such as maleic anhydride modified polybutene, have been proposed to replace the low-surface-energy perfluoropolyethers in order to maintain a continuous meniscus with reduced bouncing for contact recording [21]. A new set of magnetic recording disk lubricant additives will be needed if the perfluoropolyether is replaced by a hydrocarbon lubricant.

Acknowledgements

The authors are grateful to our many colleagues who enabled this work to be carried out. Thanks are due to H. Salehizadeh for running the motor and bearing life tests. We are thankful for the analytical support and consultation provided by J. Burns, M. Carter, R. Siemens, D. Hopper, and S. Karandikar. The co-solvent process for incorporating additives in the grease was developed by P. Brock. J. Miller carried out most of the aging tests and spectroscopy. We appreciate the encouragement and support of J. Lyerla, O. Melroy, and C. Wade.

REFERENCES

1. B Bhushan. Tribology and Mechanics of Magnetic Storage Devices, 2nd ed. New York: Springer-Verlag, 1996.
2. B Bhushan. Principles and Applications of Tribology. New York: John Wiley, 1999.
3. S Deeyiengyang, K Ono. Analysis of ball-bearing vibrations of hard disk spindles. *J Info Storage Proc Syst* 3(1-2):89-99, 2001.
4. C-PR Ku Investigation of hydrodynamic bearing friction in data storage information system spindle motors. *Adv Info Stor Proc Syst* 1:159-165, 1995.
5. C-PR Ku Dynamic characteristics of hard disk drive spindle motors—comparison between ball bearings and hydrodynamic bearings. *ASME J Trib* 118(2):402-406, 1996.
6. K Matsuoka et al. Development of FDB spindle motors for HD use. *IEEE Trans Magn* 37(2):783-788, 2001.
7. T Jintanawan, Iy Shen. Free vibration of a rotating disk pack and spindle motor system with rotating-shaft design. *J Info Stor Proc Syst* 2(3):129-139, 2000.
8. J Zhu, K Ono. A comparison study on the performance of four types of oil lubricated hydrodynamic thrust bearings for hard disk spindles. *ASME J Trib Trans ASME* 121(1):114-120, 1999.
9. Z Feng et al. A study of tribo-charge/emission at the head-disk interface. *J Appl Phys* 85(8):5615-5617, 1999.
10. RJA van den Oetelaar et al. Tribocharging phenomena in hard disk amorphous carbon coatings with and without perfluoropolyether lubricants. *J Appl Phys* 89(7):3993-3998, 2001.

11. H Kimura, Y Imai, Y Yamamoto. Study on fiber length control for ester-based lithium soap grease. *Trib Trans* 44(3):405–410, 2001.
12. WL Prater et al. Servo performance of actuator bearing greases. *Adv Info Storage Syst* 8:17–31, 1998.
13. PJ Sniegoski. Antioxidant depletion from lubricant thin layers. *Lubr Eng* 37(5):286–290, 1981.
14. S Hurley, PM Cann, HA Spikes. Lubrication and reflow properties of thermally aged greases. *Trib Trans* 43(2):221–228, 2000.
15. PM Cann et al. Grease degradation in rolling element bearings. *Trib Trans* 44(3):399–404, 2001.
16. S Boyde. Uniqema, private communication, 1999.
17. Synthetic lubricant. U.S. Patent 4,175,046 (11/20/79, PM Coant and GW Munn Jr.).
18. Amine salt of N-triazolyl-hydrocarbyl succinamic acid and lubricating oil composition containing same. U.S. Patent 4,283,296 (8/11/81, JW Nebzydoski and EL Patmore).
19. Synthetic ester lubricating oil composition containing particular T-butylphenyl substituted phosphates and stabilized hydrolytically with particular long chain alkyl amines. 4,440,657. U.S. Patent (4/3/84, SJ Metro and DD Carr).
20. Fluid-bearing apparatus. U.S. Patent 5,022,492 (6/11/91, H Ohno et al.).
21. M Yanigasawa, A Sato, K Ajiki. Lubricant design for contact recording systems. *IEICE Trans Electron* E81 C(3):343–348, 1998.
22. G Marchionni et al. Molecular interactions in perfluorinated and hydrogenated compounds: Linear paraffins and ethers. *Macromolecules* 26:1751–1757, 1993.
23. TE Karis, GW Tyndall, RJ Waltman. Lubricant bonding effects on thin film disk tribology. *Trib Trans* 33(2):249–225, 2001.
24. TE Karis et al. Oxidation chemistry of a pentaerythritol tetraester oil. *Trib Trans* 42(3):431–442, 1999.
25. A Bondi. *Physical Chemistry of Lubricating Oils*. New York: Reinhold Publishing Corp. 1951, pp 292–332.
26. NK Chakravarty. The influence of lead, iron, tin, and copper on the oxidation of lubricating oils. Part II. On the metal catalysed oxidation of oils. *J. Inst Petrol* 49(479):353–358, 1963.
27. YL Ischuk, W Butovets. Estimation of grease oxidation stability under dynamic conditions and antioxidant testing. *NGLI Spokesman* 55(4):133–138, 1991.
28. RG Shelkova et al. Kinetics of the high-temperature oxidation of hydrocarbons inhibited by metal dialkyldithiocarbamates. *Kinet Catal* (31):5, part 2, 1094–1098, 1991.
29. F Lockwood, EE Klaus. Ester oxidation—the effects of an iron surface. *ASLE Trans* 25(2):236–244, 1982.
30. Synthetic lubricant antioxidant from monosubstituted diphenylamines. U.S. Patent 5,489,711. (2/6/96, JT Lai).
31. KB Chakraborty, G Scott. Mechanisms of antioxidant action: Concentration effects of dialkyldithiocarbamates in the UV stabilization of polypropylene. *Polymer Degradation and Stability* 8(1):1–11, 1984.
32. MD Sexton. Mechanisms of antioxidant action. Part 4. The decomposition of 1-Methyl-1-phenylethyl hydroperoxide by zinc dialkyldithiocarbamates and zinc xanthates. *J Chem Soc Perkins Trans* 2(1):59–63, 1985.
33. SA1-Malaika, A Marogi, G Scott. Mechanisms of antioxidant action: Transformations involved in the antioxidant function of zinc dithiocarbamate: Part II. *Polymer Degradation and Stability* 10(3):237–245, 1985.
34. JM Palacios. Thickness and chemical composition of films formed by antimony dithiocarbamate and zinc dithiophosphate. *Trib Int* 19(1):35–39, 1986.
35. JM Palacios. Films formed by antiwear additives and their incidence in wear and scuffing. *Wear* 114:41–49, 1987.

36. YU Lozovoi et al. Chemical modification of friction surfaces: Surface layers formed in boundary friction. *Sov J Friction and Wear* 11(2):270–277, 1990.
37. JM Perez et al. Characterization of tricresylphosphate lubricating films by micro-Fourier transform infrared spectroscopy. *Trib Trans* 33(1): 131–139, 1990.
38. RL Cottingham, H Ravner. Interactions in neopentyl polynol ester–tricresyl phosphate-iron systems at 500 F. *ASLE Trans* 12:280–286, 1969.
39. RL Jones, H Ravner, RL Cottingham. Inhibition of iron-catalyzed neopentyl polyol ester thermal degradation through passivation of the active metal surface by tricresyl phosphate. *ASLE Trans* 13(1):1–10, 1970.
40. WM Cummings. Fuel and lubricant additives I. *Lubr* 63(1):1–12, 1977.
41. MR Fenske et al. Oxidation of lubricating oils. *Ind Eng Chem* 33(4):516–524, 1941.
42. RG Larsen, FA Armfield, Catalysis in the oxidation of lubricating oil. *Ind Eng Chem* 35:581–588, 1943.
43. H Diamond, HC Kennedy, RG Larsen. Oxidation characteristics of lubricating oils at high temperatures. *Ind Eng Chem* 44:1834–1843, 1952.
44. A Klinkenberg, BV Poulston. Antistatic additives in the petroleum industry. *Petroleum* 44(419):379–393, 1958.
45. LA Bronshtein, YN Shekhter, VM Shkol'nikov. Mechanism of electrical conduction in lubricating oils (review). *Chemistry and Technology of Fuels and Oils* 15(5–6):350–355 1979.
46. TP Vishnyakova et al. Fuel antistatic additives and the mechanism of their action. *Chem Tech Fuels and Oils* 16(7–8):457–61, 1980.
47. AI Belousov, EM Bushueva. Mechanism of electrical conduction in hydrocarbon liquids with antistatic additives. *Chemistry and Technology of Fuels and Oils* 19(11–12): 549–552, 1983.
48. HL Walmsley. The avoidance of electrostatic hazards in the petroleum industry. *J Electrostatics* 27:149–156, 1992.
49. Conductive lubricant for magnetic disk drives. U.S. Patent 5,641,841 (6/24/97, AF Diaz et al.).
50. Conductive lubricant for magnetic disk drives. U.S. Patent 5,744,431 (4/28/98, AF Diaz et al.).
51. Conductive lubricant for magnetic disk drives. U.S. Patent 5,886,854 (13/23/99, AF Diaz et al.).
52. Disc drive hydro bearing lubricant with electrically conductive non-metallic additive. U.S. Patent 5,940,246 (8/17/99, RU Khan et al.).
53. D Sianesi et al. Perfluoropolyethers: Their physical properties and behaviour at high and low temperatures. *Wear* 18:85–100, 1971.
54. BS Nader et al. Development and tribological properties of new cyclotriphosphazene high temperature lubricants for aircraft gas turbine engines. *Trib Trans* 35(1):37–44, 1992.
55. DJ Perettie. Cyclic phosphazenes as advanced lubricants for thin film magnetic media. In GG Adams, B Bhushan, D Miu, and J Wickert, eds. *ISPS—Vol. 1, Advances in Information Storage and Processing Systems*, ASME Book no. H01016, 1995, pp 117–123.
56. PH Kasai, Degradation of perfluoropoly(ethers) and role of X-1P additives in disk files. *J Info Storage Proc Syst* 1(1):23–31, 1999.
57. CM Mate et al. Investigation of phosphazene additive for magnetic recording lubrication. *IEEE Trans Magn* 34(4):1744–1746, 1998.
58. C-Y Chen, DB Bogy, CS Bhatia. Tribochemistry of various lubricants on CH_x coated disks using DLC coated and uncoated $\text{Al}_2\text{O}_3/\text{TiC}$ sliders in UHV. Computer Mechanics Laboratory, Department of Mechanical Engineering, University of California, Berkeley, CA, Technical Report no. 97–003, 1997.

59. M Yang, et al. Environmental effects of phosphazene lubricated computer hard disks. *IEEE Trans Magn* 30(6):4143–4145 1994.
60. Z Zhao, B Bhushan. Tribological performance of PFPE and X1-P lubricants at head-disk interface. Part I—Experimental results. *Trib Lett* 6:129–139, 1999.
61. CE Snyder, Jr. et al. Synthesis and development of improved high-temperature additives for polyperfluoroalkylether lubricants and hydraulic fluid. *Lubr Eng* 35(8): 451–456, 1978.
62. BA Shogrin et al. Evaluation of boundary-enhancement additives for perfluoropolyethers. *Trib Trans* 42:747–754, 1999.
63. Stability additive for perfluoropolyalkylethers. U.S. Patent 5,302,760 (4/12/94, LJ Gshwender and CE Snyder).
64. LJ Gshwender et al. Computational chemistry of soluble additives for perfluoropolyalkylether liquid lubricants. *Trib Trans* 39(2):368–373, 1996.
65. TE Karis, HS Nagaraj. Evaporation and flow properties of several hydrocarbon oils. *Trib Trans* 43(4):758–766, 2000.
66. I-S Rhee. Development of a new oxidation stability test method for greases using a pressure differential scanning calorimeter. *NLGI Spokesman* 55(4):7–123–16-123, 1991.
67. A Ali et al. The chemical degradation of ester lubricants. *ASLE Trans* 22(3):267–276, 1979.
68. E Cvitkovic, EE Klaus, F Lockwood. A thin film test for measurement of the oxidation and evaporation of ester-type lubricants. *ASLE Trans* 22(4):395–401, 1979.
69. J Lahijani, FE Lockwood, EE Klaus. The influence of metals on sludge formation. *ASLE Trans* 25(1):25–32, 1982.
70. DB Clark, EE Klaus, SM Hsu. The role of iron and copper in the oxidation degradation of lubricating oils. *ASLE Lubr Eng* 41(5):280–287, 1985.
71. ML Williams, RF Landel, JD Ferry. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass forming liquids. *J Amer Chem Soc* 77:3701–3707, 1955.
72. S-J Kim, TE Karis. Glass formation from low molecular weight organic melts. *J Mater Res* 10(8):2128–2136, 1995.
73. FJ Stevens. Analysis of protein-protein interaction by simulation of small-zone size-exclusion chromatography: Application to antibody-antigen association. *Biochemistry* 25:981–993, 1986.
74. PA Willermet. Some engine oil additives and their effects on antiwear film formation. *Trib Lett* 5(1):41–47, 1998.
75. TV Medvedeva et al. Evaluation of grease oxidation inhibitor efficiency by means of IR spectroscopy. *Chem Tech Fuels and Oils* 8(3–4):308–311, 1972.
76. K Inoue, H Watanabe. Interactions of engine oil additives. *ASLE Trans* 26(21): 189–199, 1983.
77. LN Sosulina et al. Micromethods for the investigation of lubricating grease composition. *Chem Tech Fuels and Oils* 16(9–10):685–688, 1980.
78. VA Zakupra et al. Chromatographic and spectrometric investigation of the composition of greases in lubricated components. *Chem Tech Fuels and Oils* 17(11–12): 704–710, 1981.
79. MS de Vries, HE Hunziker. Vacuum UV photoionization mass spectrometry of small polymers using jet cooling. *J Photochem Photobiol A: Chem* (106):31–36. 1997.
80. Magnetic recording device with spindle motor lubricant of specified amine and carbamate concentrations/ratios. U.S. Patent 5,940,247 (8/17/99. TE Karis and HS Nagaraj).
81. Magnetic recording device. U.S. Patent 6,194,360 (2/27/2001, TE Karis and HS Nagaraj).

82. H-G Elias. *Macromolecules 1: Structure and Properties*. New York: Plenum Press, 1977, 205.
83. D-H Han, M Masuko. Elucidation of the antiwear performance of several organic phosphates used with different polyol ester base oils from the aspect of interaction between additive and base oil. *Trib Trans* 41(4):600–604, 1998.
84. D-H Han, M Masuko. Comparison of antiwear additive response among several base oils of different polarities. *Trib Trans* 42(4):902–906, 1999.
85. CJ Jiaa, Y Liu, C Gao. Additive mechanism investigation of perfluoropolyether lubricants with a phosphazene additive. *Trib Trans* 43(4):659–664, 2000.
86. TE Karis. Tribochemistry in contact recording. *Trib Lett* 10(3): 149–162, 2001.
87. M Yang, FE Talke. Effects of gas composition, humidity and temperature on the tribology of the head/disk interface—Part I: Experiments. *Trib Trans* 39(3):615–620, 1996a.
88. M Yang, FE Talke. Effects of gas composition, humidity and temperature on the tribology of the head/disk interface—Part II: Model and analysis. *Trib Trans* 39(3): 691–697, 1996b.
89. MS Jesh, PR Segar. The effect of vapor phase chemicals on head/disk interface tribology. *Trib Trans* 42(2):310–316, 1999.
90. TE Karis. Water adsorption on thin film magnetic recording media. *J Coll Int Sci* 225(1):196–203, 2000.
91. M Smallen et al. The role of disk carbon and slider in water adsorption. *IEEE Trans Magn* 30(6):4137–4139, 1994.
92. W Hua et al. Probability model for slider-disk interaction. *J Info Storage Proc Syst* 1:273–280, 1999.
93. J Gui, B Marchon. A stiction model for a head-disk interface of a rigid disk drive. *J Appl Phys* 78(6):4206–4217, 1995.
94. B Bhushan, S Chilamakuri. Non-Gaussian surface roughness distribution of magnetic media for minimum friction/stiction. *J Appl Phys* 79(8):5794–5796, 1996.
95. TE Karis, VJ Novotny. Pin-on-disk tribology of thin film magnetic recording disks. *J Appl Phys* 66(6):2706–2711, 1989.
96. B Marchon, N Heiman, MR Khan. Evidence for tribochemical wear on amorphous carbon thin films. *IEEE Trans Magn* 26(1):168–170, 1990.
97. GW Tyndall, RJ Waltman, DJ Pocker. Concerning the interactions between Zdol perfluoropolyether lubricant and an amorphous-nitrogenated carbon surface. *Langmuir* 14(26):7527–7536, 1998.
98. Q Zhao, HJ Kang, FE Talke. Effect of phosphazene-type additive X-100 on the tribological performance of Z-Dol at the head disk interface. *Lubr Eng* 57(2):15–20, 2001.
99. R Pit et al. Formation of lubricant “moguls” at the head/disk interface. *Trib Lett* 10(3): 133–142, 2001.
100. J Gui, B Marchon. Fly/stiction: Mechanical instability of a head-disk interface. *IEEE Trans on Magn* 34(4):1804–1806, 1998.
101. A Khurshudov, P Baumgart, RT Waltman. In situ quantitative analysis of nano-scale lubricant migration at the slider-disk interface. *Wear* 229:690–699, 1999

Additives for Grease Applications

ROBERT SILVERSTEIN

The Orelube Corporation, Plainview, New York, U.S.A.

LESLIE R. RUDNICK

The Energy Institute, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.

1 INTRODUCTION

Greases are one of the oldest forms of lubricating materials, and in fact, the first greases can be considered environmentally friendly and biodegradable by our modern conventions. Ancient Egyptians about 1400 B.C. made crude greases to lubricate the wheels of their chariots. These early greases consisted of both mutton fat and beef fat, which were sometimes mixed with lime. In fact, the word “grease” is derived from *crassus*, the Latin word for fat. As time progressed there was only minimal improvement in grease performance until about the 18th century. During the 18th and 19th centuries and the Industrial Revolution, society created a greater variety of new machines. This modern technology that developed during and after the Industrial Revolution required lubricants to handle greater loads and to operate under more severe conditions. New grease technology was needed to improve the performance of equipment and to improve the life time of machine components.

Grease is a semisolid or solid lubricant composed of a thickening agent dispersed in a liquid lubricant, or in combination of lubricants. The principal advantage of choosing grease over conventional lubricating oil in certain applications is because of grease’s ability to remain in contact with the desired moving surfaces. Grease will generally not leak away from the point of application. Thickeners in the grease are designed to reduce any migration caused by gravity, pressure, or centrifugal action. Grease is best thought of as thickened oil.

There are at least three main reasons where grease is chosen over oil as a lubricant:

- In applications where leakage of oil would occur
- Where the natural sealing action of grease is needed
- When greater film thickness is necessary for the application

The liquid lubricant or base oil in grease usually accounts for 70–95% of the grease. The base oil may be mineral oil, synthetic, or natural oil, such as a vegetable oil. Oils from animal sources are generally not used today. Generally between 5–25% of the grease composition is thickening agents. The most common thickeners in use today are metallic soaps, particularly lithium soaps, which account for over 60% of the grease market. Silica, expanded graphite [1], or clays (bentonite or hectorite) are sometimes used as thickeners. Clay thickeners represent about 5–10% of the grease market.

Additives, required to improve certain properties of the grease such as oxidative stability, wear protection, and corrosion inhibition, are used in 0.5–10% of the grease depending on the grease type and application. When grease is to be used under more severe conditions, it generally contains a more enhanced additive package. These additives are often the same additives used in liquid lubricants. Exceptions are solid additives such as graphite and molybdenum disulfide, which are typically used as antifriction and extreme-pressure (EP) additives.

Further research will continue to provide newer and more effective components that will serve as thickeners and/or additives in the field of lubrication. These future materials are expected to provide greases and liquid lubricants with properties and performance capabilities exceeding those possible today.

In addition to the resistance to flow that maintains grease at the point of application, the primary performance features are to reduce friction and wear. Some of the main factors that affect grease properties and performance are

- Type and amount of thickener
- Consistency or hardness
- Dropping point
- Antioxidant additives
- Extreme pressure additives
- Pumpability
- Volatility
- Environmental considerations such as toxicity and biodegradability

Soaps, used as thickeners, can be considered additives in greases, even though they generally comprise a large percentage of the grease composition. Thickeners are, in fact, what make grease grease and what differentiate grease from conventional lubricating fluid. This chapter does not consider soaps, because they have been previously described by Klamann [2] and Boner [3]. Functionalized soaps have also been used to impart extreme-pressure and antiwear performance to grease [2].

The purpose of this chapter is to serve as a review of some of the important additives used in greases and to present a variety of additive testing results that demonstrate their performance benefits. Because final grease formulations are a function of particular performance needs, application data described herein are focused on base oil/thickener/additive effects and not on fully formulated greases, many of which are proprietary.

2 WORLDWIDE USE OF GREASES

On a global basis, the region that consumes the largest percentage of the world's grease is North America (541MM pounds). Europe (400MM pounds), Japan (137MM pounds), and Asia Pacific (63.5MM pounds) represent the remaining bulk of the global grease production. Each of the world's different regions requires different grease products.

The NLGI Grease Production Survey Report for the year 2000 [4] reports a grand total of approximately 1.5 billion pounds of lubricating grease manufactured worldwide. Of this, conventional lithium soap and lithium complex were approximately 53% and 15% of the total, respectively. Aluminum complex and polyurea were approximately 5%, calcium soap approximately 14%, and organoclay approximately 3.5%.

In the United States and Canada, conventional lithium and lithium complex greases represent 38% and 30%, respectively, of the 541 million pounds of grease produced in 2000. Polyurea and aluminum soap greases each represent about 7.6 and 9%, respectively, of this volume, with calcium soap and organoclay thickeners at about 6% and 7.5%, respectively, of the production. Highly refined, chemically modified mineral oils (CMMO) or synthetic base oils are used in high-performance greases in more demanding applications that cannot be met with conventional greases [4]. Industrial applications comprise the majority of grease used worldwide; the largest application areas are found in railroad lubrication, steel production, and general manufacturing. Automotive applications include trucks, buses, agricultural and off-road construction equipment, and passenger cars [5].

3 PRODUCTION OF GREASES

Soap-thickened greases are manufactured using three basic sequential process steps. First, the soap is formed by the saponification of various fats. Then the soap is dehydrated and further optimized in properties. Finally, milling to provide a consistent dispersion of all components disperses the soap, base fluid, and additives. Milling is a process of shearing the grease to disperse all components. Brown et al. have demonstrated how the process of shearing during milling orients the soap fibers [6]. Dispersion and orientation can harden greases by 100 penetration units [7].

Grease is produced using a kettle process, a contactor process, or a continuous process. These processes differ in terms of the rate of grease production, the quantity of grease to be produced, and the initial investment in equipment. The kettle and contactor processes are both batch processes. The contactor process utilizes pressure to reduce reaction time.

When grease is prepared using a batch process, the base oil is heated together with the additives and thickening agents. If saponification of the fat is required to form soap, the reaction mixture is brought to a higher temperature to complete the reaction and to fully disperse all components. A typical batch kettle reaction will take 8 to 24 hr and can range in scale from 2 to 50,000 lb. They are typically cylindrical in shape with a height-to-diameter ratio of 1–1.5. They can have dished or conical bottoms and either flat or dished tops. Because the principal objective in making grease is the dispersion of components, kettles may have either one set of rotating

paddles or an arrangement of stationary and rotating paddles so as to more efficiently mix the components. Scrapers are sometimes used to remove material adhering to the kettle walls.

The advantages of the contactor process are reduced heating and reaction time. For example, a typical 20,000-lb batch of lithium grease may take 20hr in a kettle process, but only 5 to 7 hr in a contactor process [8,9]. In the contactor process, fatty acids or glycerides such as hydrogenated castor oil, tallow or vegetable oils, and, for example, lithium hydroxide are added at the top. Base fluid is added and water may also be added. The contactor is pressurized, which accelerates the process of saponification. Other process steps include cooling after reaction, adding additional finishing oil, and pumping the grease to a finishing kettle.

There are three main sections in a continuous grease reactor: the soap reactor section, a dehydration section, and a finishing section. Saponification occurs in the reactor section, where the fatty component, alkali, and base fluids are added. The grease components are transferred to the dehydration section, which operates under a vacuum to remove volatiles. The product at this stage is a dehydrated soap base. The product of the dehydration section is moved to the finishing section, where additional base fluid and additives are combined and dispersed [10]. A comparison of the continuous and kettle processes is shown in Table 1 [8].

Many chemical and manufacturing factors can affect the properties and performance of greases. For example, several factors that affect the manufacture of lithium complex greases include the base fluid, fatty acid concentration, temperature, moisture, and additive chemistry [11]. Several features of the various manufacturing processes need to be considered in preparing greases. These include the yield of the grease product, any energy requirements to prepare the grease, production time, and capital investment along with associated maintenance costs.

For applications in extreme environments, such as aerospace and military, specialized lubricating greases are necessary. These greases must be able to perform reliably under conditions that most other greases never experience. These materials must have excellent thermal stability, have low volatility, and be able to function under very low and very high temperature regimes. The base fluid and all additive components must meet these criteria. For example, high-performance greases have been made that incorporate multiply alkylated cyclopentanes (MAC) as the base fluid [12]. Other specialized base fluids have been studied, including those containing fluorine and other heteroatoms.

Table 1 Comparison of Continuous and Kettle Grease Processing

	Continuous process	Kettle process
Investment cost factor	1.0	1.2
Manufacturing cost factor	1.0	4.1
Heat load (Btu/hr)	1,500,000	3,000,000
Cooling water (gal/min)	75	200
Electrical use (kW/hr)	120	380

Note: Values are based on a 10 million lb/yr output of lithium, calcium, and sodium greases.

4 GREASE COMPOSITION AND PROPERTIES

4.1 Composition

Base fluids used in conventional grease are of three types: mineral (petroleum-derived), synthetic (synthesized from discrete chemical components), and natural (plant- and animal-derived). Mineral oils can be paraffinic or naphthenic. Synthetic base fluids commonly used include polyalphaolefins (PAOs), esters, polyglycols, and silicones. Natural oils can be derived from soybean, rapeseed, and other plant oils and high-oleic acid versions of these oils.

Base fluid viscosity, in general, directly affects the viscosity characteristics of the resultant grease. Base fluids used in grease formulation generally range from 150N to 600 N oils and may also include Bright Stock. High-viscosity base fluids are typically used for high-temperature, heavy-duty applications. Alternatively, high-speed applications generally require low-viscosity oils. Lubricating greases are also classified according to thickener type [13].

There are many different types of grease thickeners; however, a few major types are generally employed throughout the industry, depending on the application. Alkali components include lithium hydroxide, calcium hydroxide, sodium hydroxide, and aluminum hydroxide. These alkalis are reacted with materials from animal, marine, and vegetable sources. Nonsoap thickeners can also be used. These include silica, clays, urea, polyurea, and Teflon.®

Grease stability, oxidation resistance, effects of water, maximum operating temperature, and other properties have been summarized by Wills [13].

4.2 Properties

Grease is generally classified and evaluated for properties and performance using tests in the following categories:

- Consistency
- Stability
- EP/AW
- Pumpability
- Corrosion
- Water tolerance
- Bench performance tests

4.3 Consistency

One of the most important properties of grease is its consistency. Just as lubricating oils are available in different viscosity grades, greases are specified in terms of their consistency, as measured by their ASTM “worked penetration.” “Worked penetration” means that the grease is “worked” for 60 strokes in a standard manner before measurement. Penetration is measured by distance, in tenths of millimeters, that a standard cone will penetrate a grease sample when a standard force is applied. The standard method of measurement is ASTM D 217 [7]. However, a special procedure, ASTM D 1403, has been designed to utilize one-quarter and one-half scale

cones for smaller samples [14]. Equations have been developed to convert the results to compare to ASTM D 217 results.

In these tests, which are performed at a constant temperature of 25°C (77°F), a harder grease will exhibit a lower penetration number than a softer grease. The National Lubricating Grease Institute (NLGI) classification system (see Table 2) ranks grease hardness based on this test.

Other tests include Apparent viscosity (ASTM D 1092) and Evaporative loss (ASTM D 972 and D 2595).

4.4 Stability

4.4.1 Dropping Point

The hardness of grease is a function of temperature. Greases act as thickened lubricants only to a point, and then at some temperature they become fluid. A standard measure of the resistance of a grease to flow as temperature is increased is the Dropping Point (ASTM D 2265) [15]. In essence, the dropping point is the measure of the heat resistance of the grease. In the dropping point test, a grease sample is packed into a standard test cup with a small opening. The sample is heated by introducing the sample into a preheated aluminum block. The sample temperature plus one third of the difference between that temperature and the block temperature when the first drop of fluid leaves the cup is defined as the dropping point. Guidelines for the maximum usable service temperature and ranges for dropping points of greases made with various thickeners are summarized in Table 3 [16,17]. The self-diffusion of oil in lubricating greases has been studied using nuclear magnetic resonance spectroscopy at temperatures between 23°C and 90°C. Greases based on naphthenic mineral oils and polyalphaolefin synthetic oils were measured. It was shown in this temperature range (40–90°C) that, using the same base fluid, the concentration of the thickener affected diffusion [18].

Other measures of high-temperature stability include High Temperature Bleed (ASTM D 1742), Trident Probe (ASTM D 3232), Cone Bleed (FTM 791B), Evaporation (ASTM D 972 and D 2595), Rolling Stability (ASTM D 1831), Oxidative Stability (ASTM D 942) and a High Speed Bearing Test (ASTM D 3336).

Table 2 NLGI Classification System for Penetration of Greases

NLGI grade	Worked penetration
000	445–475
00	400–430
0	355–385
1	310–340
2	265–295
3	220–250
4	175–205
5	130–160
6	85–115

Table 3 General Temperature Properties of Various Thickened Greases

Thickener	Dropping point (°F)	Maximum usable service temperature
Aluminum soap	230	175
Calcium soap	270–290	250
Sodium soap	340–350	250
Lithium soap	390	275
Calcium complex	>500	350
Lithium complex	>500	350
Aluminum complex	>500	325
Polyurea (nonsoap)	>450	350
Organoclay (nonsoap)	>500	350

4.5 Extreme Pressure/Antiwear (EP/AW)

4.5.1 Four-Ball Wear

ASTM D 2266 describes a test method using three hard steel balls in a locked position and coated with lubricating grease. A fourth ball is rotated against the three stationary balls, producing a wear scar on each of the three balls, which is reported as the average scar diameter. This test is run at light loads; thus seizure or welding does not occur [19].

4.5.2 Four-Ball EP

ASTM D 2596 describes a test method similar to ASTM D 2266 except that the loads are much higher. At a certain load, the four balls will weld together; this is referred to as the weld load. The weld load can be used to assess whether lubricating grease has a low, medium, or high level of load-carrying ability. The ASTM defines the load wear index (or the load-carrying property of the lubricant) as an index of the ability of a lubricant to prevent wear at applied loads. Under the test conditions, specific loadings in Newtons (kg-force) having intervals of approximately 0.1 logarithmic units are applied to three stationary balls for ten runs prior to welding. The load wear index is the average of the corrected loads determined for the ten applied loads immediately preceding the weld point [20].

Fretting wear is measured using ASTM D 3704, and load-carrying capacity can be evaluated using Timken O. K. Load (ASTM D 2509).

4.6 Pumpability

Pumpability can be evaluated using a USS Low-Temperature Mobility test. It is largely a function of thickener type and concentration and is not significantly affected by additives.

4.7 Corrosion

Three common tests for corrosion are a Copper Corrosion Test (ASTM D 130) modified for grease, a Bearing Rust Test (ASTM D 1743), and the Emcor Rust Test.

4.8 Water Tolerance

Water Washout is measured using ASTM D 1264. Water Spray-off is measured using ASTM D 4049. The Wet Roll Stability of grease is evaluated using a modified ASTM D 1831 test.

4.9 Bench Performance Tests

Several bench performance tests are used in the grease industry to evaluate greases prior to field evaluation. Some of these include a High-Temperature Wheel Bearing Test (ASTM D 3527), an SKF R2F Test that simulates paper mill applications, the FE-8 Test, CEM Electric Motor Test, and a GE Electric Motor Test. Low-Temperature Torque is evaluated using ASTM D 1478, and ASTM D 4693 at a temperature of -54°C .

5 GREASE THICKENERS

Most grease is made from metal-salt soaps that serve as the thickeners for the base fluid. Metal-salt soap thickeners are prepared from alkali base and a fat or fatty acids. The fatty materials may be derived from animal, marine, or vegetable fatty acids or fats. Fatty acids from these sources are generally even-numbered, straight-chain carboxylic acids containing zero or one double bond. A common fat used for making grease is hydrogenated castor oil, which yields lithium 12-hydroxy stearate upon saponification. Lithium hydroxide, calcium hydroxide, aluminum hydroxide, and sodium hydroxide are frequently used as the alkali materials. Sample reactions for the formation of some of these soaps are shown in Figure 1 [2].

In modern greases, simple soaps and complex soaps are used. A simple soap is prepared from one fatty acid and one metal hydroxide. NLGI defines complex grease as soap wherein the soap crystal or fiber is formed by co-crystallization of two or more compounds: the normal soap and the complexing agent [21]. The normal soap is the metallic salt of a long-chain fatty acid similar to a regular soap thickener, e.g., calcium stearate and lithium 12-hydroxy stearate. The complexing agent can be the metallic salt of a short-chain organic acid, e.g., acetic acid.

In summary, grease thickeners are generally one of the following types:

- Aluminum
- Aluminum complex
- Calcium
- Calcium complex
- Lithium
- Lithium complex
- Polyurea
- Clay

The properties of complex-soap greases depend on [22]

- Metal type (lithium, calcium, etc.)
- Normal soap type (metallic stearate, metallic 12-hydroxystearate, etc.)
- Complexing agent type (metallic acetate, benzoate, carbonate, chloride, etc.)

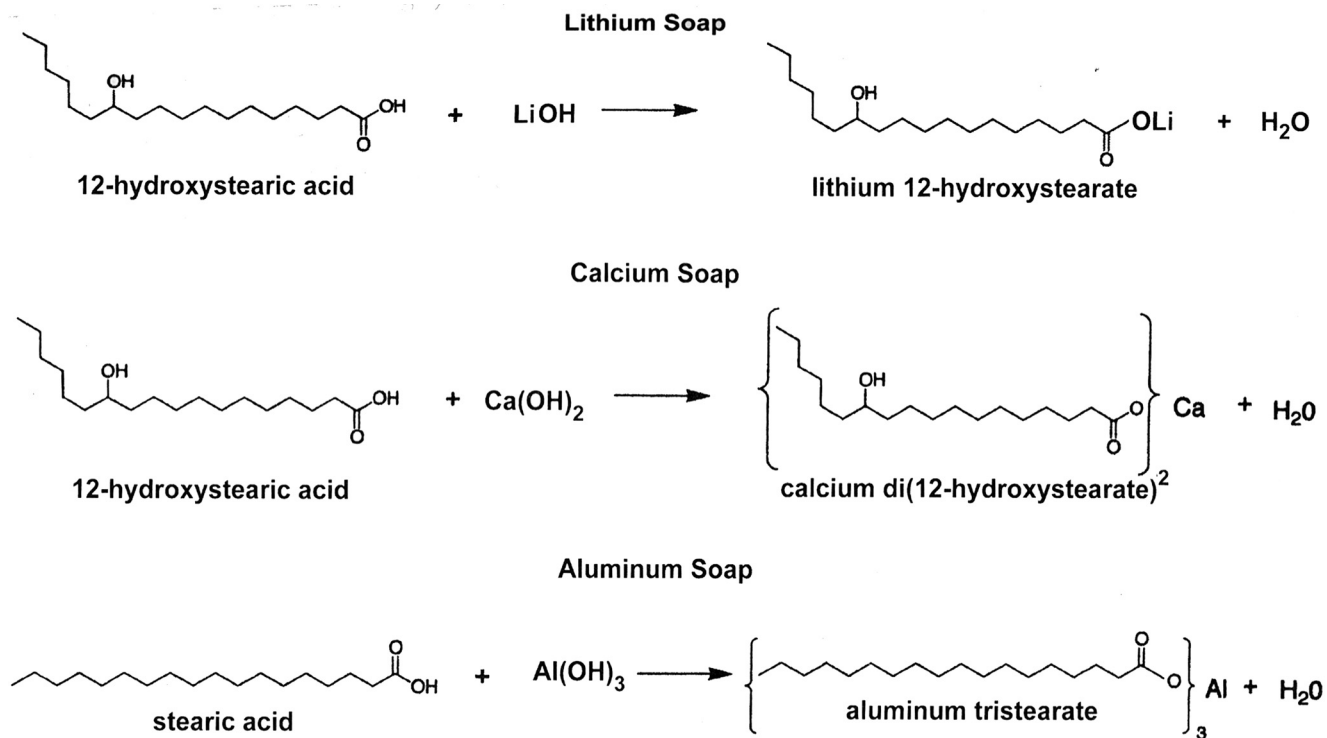


Figure 1 Chemical reactions for preparation of grease thickeners.

- Normal soap to complexing agent ratio and
- Manufacturing conditions

Complex greases can be used over a greater temperature range because they have higher dropping points than normal greases.

The structure of grease thickeners directly affects the properties and performance characteristics of fully formulated grease. Thickeners range in structure from linear soaplike structures to more complex circular structures. Physically, they may be needles, platelets, or spherical and can vary significantly in dimension. Soaps form microscopic fibers, which form a matrix to hold the base fluid. Fibrous sodium soap structures can be 1×100 microns, whereas short-fibered lithium soap might be on the order of 0.2×2 microns. Aluminum soaps might have a diameter of only 0.1 micron [23]. Boner has reported that the rheological properties of lithium-based grease depend on the different fiber dimensions of the soap molecules [24]. Fiber structure and the surface area-to-volume ratio of the fibers tend to vary with different soaps. It has been reported that a thin strip is the most effective shape for a thickener molecule. With increase in the surface-to-volume ratio of the thickener molecules, the grease structure is strengthened as indicated by lower penetration [25]. Wilson has reported that lithium soap fibers are long, flat strips [26]. In general, sodium soap fibers range in size from 1.5–100 microns, and lithium soap fibers from 2–25 microns. Aluminum soap fibers are essentially spherical on the order of 0.1 microns. Calcium soap fibers are short, generally about 1 micron long. Organophilic bentonite is about 0.1×0.5 microns.

In general, it is safe to conclude that greases made with different grease thickeners should not be mixed in the same application. This could result in poorer performance of the mixed greases relative to that expected from either individual grease. Incompatibility and poorer performance could also result in equipment malfunction. For example, it is generally cautioned that lithium and sodium greases are incompatible. There are always two sides to every story, and Meade, in an extensive study, tested more than 1200 grease combinations and found 75% of them to be compatible [27].

The type and structure of the grease thickener affect the stability of the grease during and after shear forces are applied. In bench tests, lithium-thickened greases have been shown to have the least reduction in shear stress and in film thickness. Less structural resistance was found for calcium-, sodium-, and bentonite- (clay-) thickened greases [28]. Performance features and application of greases as a function of the types of thickener are summarized in [Table 4](#) [2].

Greases are like other lubricants in that they exhibit limited useful lifetimes. The length of time that grease maintains the property and performance criteria for which it was designed depends on all the factors affecting other lubricants. In addition, grease structure is affected by the thermal, mechanical, and oxidative stresses related to the thickener structure. As grease ages, it may become dry and brittle under the conditions of the application and, therefore, will not exhibit the lubricating properties and performance for which the grease was originally designed.

The general performance and properties of grease as a function of thickener are as follows:

1. An aluminum soap-thickened grease generally exhibits excellent water resistance, poor mechanical stability, excellent oxidative stability, good

Table 4 Performance Features and Applications of Greases as a Function of Thickener

Thickener	Performance features	Applications
Aluminum soap	Low dropping point; excellent water resistance	Low-speed bearings; wet applications
Calcium soap	Low dropping point; excellent water resistance	Bearings in wet applications; railroad rail lubricants
Sodium soap	Poor water resistance; good adhesive properties	Older industrial equipment requiring frequent relubrication
Lithium soap	Higher dropping point; resistance to softening and leakage; moderate water resistance	Automotive chassis; automotive wheel bearings; general industrial grease
Calcium complex	Excellent water resistance; inherent EP/load-carrying capability	High-temperature industrial and automotive bearing applications
Lithium complex	Resistance to softening and leakage; moderate water resistance	Automotive wheel bearings; high-temperature industrial rolling-element applications
Aluminum complex	Excellent water resistance; resistance to softening; good pumpability; reversibility	Steel mill roll neck bearings; rolling-element and plain bearings; high-temperature industrial applications; food processing machinery
Polyurea (nonsoap)	Good water resistance; oxidation resistant; less resistance to softening and leakage	Industrial rolling-element bearings; automotive constant velocity joints
Organoclay (nonsoap)	Resistance to leakage; good water resistance; thickener has no melting point	High-temperature bearings with frequent relubrication

oil separation, poor pumpability, and in general can be used to a maximum application temperature of 175°F (79.5°C).

2. A calcium soap-thickened grease generally exhibits excellent water resistance, fair mechanical stability, poor oxidative stability, excellent antirust performance, fair pumpability, and in general can be used to a maximum application temperature of 250°F (121°C).
3. A lithium soap-thickened grease generally exhibits good water resistance, excellent mechanical stability, good to excellent oxidative stability, poor to excellent antirust performance depending on the formulation, fair to excellent pumpability, and in general can be used to a maximum application temperature of 275°F (135°C).
4. An aluminum complex soap-thickened grease generally exhibits excellent water resistance, good to excellent mechanical stability, good pumpability,

and in general can be used to a maximum application temperature of 350°F (177°C).

5. A calcium complex soap-thickened grease generally exhibits excellent oil separation and good mechanical stability, the thickener in this case provides a degree of antiwear and extreme-pressure protection, and in general it can be used to a maximum application temperature of 350°F (177°C).
6. A lithium complex soap-thickened grease generally exhibits excellent oil separation, moderate water resistance, and in general can be used to a maximum application temperature of 350°F (177°C).
7. Clay-thickened grease has good to excellent water resistance, good pumpability, excellent oil separation, and in general can be used at maximum application temperatures greater than 350°F (177°C).
8. Polyurea-thickened grease has excellent oxidative stability, excellent pumpability, and excellent oil separation, but has poor worked stability and fair to modest antirust performance. These greases can be used at a maximum application temperature of 350°F (177°C). Polyurea greases soften easily, but are reversible.

Chemical and physical processes caused by thermal and shear stresses degrade greases [29]. These authors demonstrated that thermally aged lithium hydroxystearate greases were affected in terms of oil film thickness and oil release in a rolling contact under starved conditions.

6 OXIDATION INHIBITORS

The mechanism of hydrocarbon oxidation, because of its importance to lubricant chemistry and performance, has been well studied and is reviewed in [Chapter 1](#) of this book.

Hydrocarbons react with oxygen to initially produce peroxides and hydroperoxides that further react to give alcohols, aldehydes, ketones, and carboxylic acids. These oxidation reactions proceed via free-radical chain processes. Grease, which is basically soap-thickened hydrocarbon, is also susceptible to oxidation. In addition, the metals of the metal soaps can catalyze oxidation.

Examples of classes of antioxidants used in grease are

- Hindered phenols: e.g. 2,6-di-*t*-butyl phenol and 2,6-di-*t*-butyl-*p*-cresol
- Aromatic amines: e.g., diarylamines, di-octyldiphenylamine
- Metal dialkyldithiophosphates: e.g., zinc dithiophosphate
- Metal dialkyldithiocarbamates: e.g., zinc and molybdenum dithiocarbamates
- Ashless dialkyldithiocarbamates
- Sulfurized phenols: e.g., phenolic thioesters and phenolic thioethers
- Phenothiazine
- Disulfides; e.g., diaryldisulfides
- Trialkyl and triaryl phosphates and phosphites: e.g., tris(di-*t*-butyl phenyl phosphite)

Alkylated phenol antioxidants are most effective at low temperatures. Secondary aromatic amines such as phenyl alpha-naphthylamine (PANA), phenyl beta-naphthylamine (PBNA), di-octyldiphenylamine, and phenothiazines are most useful at high temperatures [5]. In practice, grease is generally formulated to include a combination of alkylated or secondary amine-type and phenol-type antioxidants to provide performance over as wide a temperature range as possible.

In some cases the combination of antioxidants (or other additives) provides an additive effect, while in other cases synergy is observed when both a hindered phenolic and an aryl amine antioxidant are used together in the same formulation.

7 FRICTION AND WEAR

Friction is the force required to cause the motion of two surfaces or bodies in contact with each other. Lubricants are used to reduce the frictional forces. High friction results in heat and because more force or power is necessary to move the parts relative one another, this friction reduces operating efficiency. When the lubricant film is insufficient to protect the metal surfaces, there is wear on one or both components. Wear is material loss directly caused by the interaction of asperities on the two surfaces while in relative motion to each other. Since wear results in the loss of material and the scarring changes the size and shape of the machined components, wear reduces the useful life of the components. Extreme wear can result in failure of the equipment and in safety issues. There are three general types of wear: abrasive, adhesive, and corrosive. These are generally addressed by formulating a grease using additives designed to protect against these phenomena. When a lubricant is applied between the rubbing surfaces, the friction and wear can be minimized. Three lubrication regimes are defined depending on the amount of lubricant film separating the surfaces. These are

- Boundary lubrication
- Elasto-hydrodynamic (mixed lubrication)
- Hydrodynamic lubrication

These three lubrication regimes are indicated on a Stribeck curve shown in [Figure 2](#) [30]. Approximate thickness of films in each regime and how they are related to the size of asperities and sliding wear debris in the boundary regime are shown in [Table 5](#) [31].

Hydrodynamic lubrication is a regime where the moving surfaces are essentially separated from each other. In this regime the viscosity of the oil in combination with the motion of the mechanical components can produce a fluid pressure high enough to completely separate the two surfaces.

Elasto-hydrodynamic lubrication is a regime where the film thickness is insufficient to completely separate the surfaces. In this regime the surface asperities make contact, which leads to wear. Lubricant in the contact area is continually replenished at the front of the contact [32]. The film thickness in the elasto-hydrodynamic regime is larger than in boundary lubrication but smaller than the film thickness in the hydrodynamic regime.

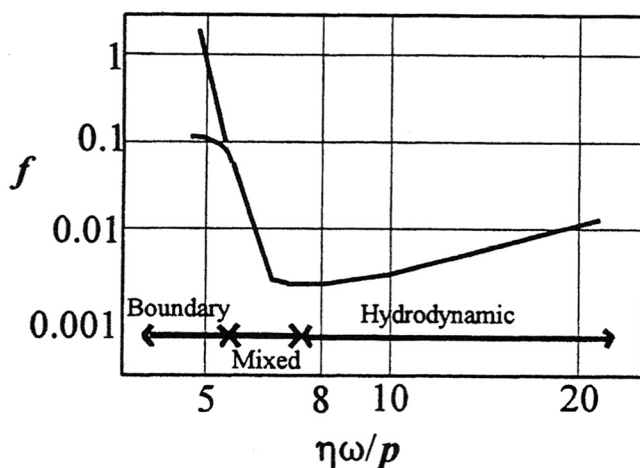


Figure 2 Stribeck curve for a journal bearing.

Boundary lubrication is a regime where film thickness between the moving surfaces is only a few molecules thick. In this regime, because of the closeness of the moving surfaces, friction and wear are determined by properties of both the surfaces and the lubricant. Boundary films form because they reduce the surface energy and, therefore, are thermodynamically favored [33]. These films form by molecules that contain polar functional groups. Because of this, they orient onto the surface by either chemical or physical adsorption. Even oxidation products derived from the breakdown of the lubricating fluid can adsorb onto metal parts and into contact areas that are being lubricated. Boundary lubrication can range from mild to severe conditions.

Physical adsorption is a reversible process where molecules adsorb and desorb from a surface without chemical change. Additives that provide protection by physical adsorption are polar structures. This is because at least two phenomena must occur: the molecule must have a preferential affinity for the surface and it should

Table 5 Dimensions of Films, Asperities, and Debris Related to Boundary Lubrication

	Approximate size range (μm)
Mono-molecular layer	0.002–0.2
Sliding wear debris	0.002–0.1
Boundary film	0.002–3
Elasto-hydrodynamic film	0.01–5
Asperity height	0.01–5
Rolling wear debris	0.07–10
Hydrodynamic film	2–100
Asperity tip radius	10–1000
Concentrated contact width	30–500

have a preferred orientation on the surface so that a more closely packed arrangement can be achieved. Alcohols, acids, and amines are examples of long-chain molecules with functional groups at the end. Molecules that can pack tightly and orient in a close packed arrangement relative to the surface provide improved film strength. Because the forces involved in physical adsorption are relatively weak, these films are effective at low to moderate temperatures. New molecules from the bulk lubricant are constantly available to replace those that physically desorb or are mechanically removed from the surface.

Chemical adsorption, however, is an irreversible process where a lubricant fluid molecule or additive component reacts with the surface to form a low shear strength protective layer. As this new low shear strength material is worn away, additional additive reacts to form a new protective layer. Protection from chemical adsorption occurs at higher temperatures because chemical reactions are required to generate the actual species that form the surface films. Extreme-pressure (EP) additives can protect lubricated surfaces at temperatures as high as 400°C.

Wear protection and friction reduction over a wide temperature range can be achieved by combining additives that function by physical adsorption and chemical adsorption. Between the low-temperature physically adsorbed layer and the high-temperature chemically adsorbed layer can be a temperature range over which there is poorer wear protection. This has been experimentally demonstrated where oleic acid was used as the normal wear additive and a chlorinated additive provided extreme-pressure protection at the higher temperatures [34].

8 EXTREME-PRESSURE (EP) AND ANTIWEAR AGENTS

Extreme-pressure and antiwear additives are used to reduce friction and prevent wear under moderate to more severe boundary lubrication conditions. Reactive compounds containing sulfur, phosphorus, or chlorine, metals, or combinations are known to provide extreme-pressure protection.

Under high loads, opposing metal surfaces contact each other, and as a result, high local temperatures develop, enabling an extreme-pressure (EP) agent to react with the metal surfaces, forming a surface film preventing the welding of opposing asperities [35].

Some of the major groups of materials that have been used as extreme-pressure and antiwear additives are as follows:

- Sulfurized olefins, fats, and esters
- Chlorinated paraffins
- Metal dialkyldithiophosphates: including antimony and zinc
- Phosphate and thiophosphate esters: e.g., tricryl phosphate, di-*n*-octyl phosphite, isodecyl diphenyl phosphite
- Ammonium salts of phosphate esters
- Borate esters
- Metal dithiocarbamates: including antimony
- Metal naphthenates: including bismuth and lead
- Metal soaps: including lead
- Sulfides and disulfides: e.g., diaryldisulfides
- High-molecular-weight complex esters

8.1 Solid Additives

Solid additives are organic or polymeric solid materials or inorganic compounds used to impart extreme-pressure and friction reduction properties to the grease, and protection in case of lubricant loss. A more detailed description of solid additives can be found in [Chapter 6](#) of this book. Examples include

- Bismuth has recently been reported as being more environmentally friendly than lead for application as an extreme-pressure additive [36,37]
- Boron-containing additives: boric acid, borax, and metal borates
- Boron nitride
- Molybdenum disulfide
- Inorganic-sulfur-phosphorus additive: patented blend of phosphate and thiosulfate [38]
- Fluorinated polymers, e.g., perfluorinated polyolefins
- Graphite—in various forms. The merits of expanded graphite have been reported [39]
- Calcium acetate, carbonate, and phosphate, cerium fluoride
- Zinc stearate, zinc oxide
- Copper powder
- Nickel powder
- Phosphate glasses

EP properties and the mechanism of phosphate glasses in lubricating greases have been studied where the authors compared phosphate glasses to molybdenum disulfide, graphite, molybdenum dithiocarbamate, polytrifluoroethylene, and boron nitride [40]. Improvement in the load-carrying capacity of greases using phosphate glass—a white, relatively inexpensive powder compared with other solid additives—has been reported to provide very effective wear protection under severe conditions [41, 42]. Under light loads, the finely divided phosphate glass particles were found to maintain their original round shape. The particles were performing as micro ball bearings under these low-load conditions. At very high loads, the phosphate glass particles compressed and formed a thick protective film on the wear surface.

Another area where greases find application is in space applications, where these lubricants need to demonstrate long-term use in situations involving vacuum. Additives used in these greases must have low volatility and excellent lubricity. Greases for these applications have included perfluoropolyalkylether (PFPAE) fluids for many years. Studies using deep-groove ball bearings filled with PFPAE-based grease have been reported with long run periods in vacuum of 10^{-4} to 10^{-5} Pa at 2000 rpm [43].

9 RUST AND CORROSION INHIBITORS

Rust is a form of corrosion formed by electrochemical interaction between iron and atmospheric oxygen and is accelerated in the presence of moisture due to the catalytic action of water [44]. Rusting of iron and steel surfaces can reduce operating efficiencies and cause part and equipment damage.

The electrochemical oxidation of the surfaces of iron or steel can be prevented by the addition of specific water-blocking additives to lubricating grease that inhibit the

formation of rust (or iron oxides). Rust inhibitors are typically highly polar surface-active oil-soluble compounds that attach to metal surfaces by physical adsorption.

Rust inhibitors incorporated into lubricating grease provide a protective film against the effects of moisture, water, and air. Corrosion inhibitors work by neutralizing corrosive acids formed by the degradation of base fluids and lubricant additives.

Examples of various chemical classes of rust and corrosion inhibitors used in grease are

- Carboxylic acids, including fatty acids: e.g., alkyl succinic acid half ester, and nonyl phenoxy acetic acid
- Salts of fatty acids and amines: e.g., disodium sebacate
- Succinates: e.g., alkyl succinic acid half ester
- Fatty amines and amides
- Metal sulfonates: including ammonium, barium, and sodium
- Metal naphthenates: including bismuth, lead, and zinc
- Metal phenolates
- Nitrogen-containing heterocyclic compounds: e.g., substituted imidazolines
- Amine phosphates
- Salts of phosphate esters

9.1 Metal Deactivators

These materials reduce the catalytic effect of metals on the rate of oxidation. They act by forming an inactive film on metal surfaces by complexing with metallic ions. Several classes of materials have been reported to be effective:

- Organic complexes containing nitrogen or sulfur, amines, sulfides and phosphates
- Derivatives of 2, 5-dimercapto-1, 3, 4-thiadiazole
- Triazoles, benzotriazoles, and tolyltriazoles
- Disilacylidene-propanediamine

9.2 Tackiness Additives

Grease may be formulated to withstand the heavy impact common in heavy equipment applications. The adhesive and cohesive properties of grease can be improved to resist throw-off from bearings and fittings, while providing extra cushioning to reduce shock and noise through the use of tackiness agents. The water resistance of such grease can also be significantly improved through the use of tackiness additives.

High-molecular-weight polymers such as polyisobutylene (PIB), polybutene, ethylene-propylene (OCP) copolymer, and latex compounds are typical examples of tackiness additives. Like all long-chain polymers, tackiness additives are susceptible to breakdown when exposed to high rates of shear. A further discussion of these interesting materials is described in [Chapter 12](#) of this book.

10 ENVIRONMENTALLY FRIENDLY GREASE

Fully formulated grease that combines needed high-performance features with environmental safety and compliance have been developed not only for civilian industrial and automotive applications but for the military as well [45].

The goal of environmentally friendly lubricants is to minimize or eliminate any potential harm or damage to humans, wildlife, soil, or water. Depending on the nature of the application, the use of environmentally friendly (or "green") lubricants will enable industry to reduce some of, and perhaps even eliminate, the costs associated with the remediation and disposal of nonbiodegradable and/or toxic lubricants.

One key raw material used in formulating biodegradable grease is vegetable oil. Vegetable oils are obtained from renewable sources and are biodegradable and, as such, are more environmentally friendly than conventional mineral oil-based lubricants [46].

A special class of vegetable oils, containing a high oleic content (greater than or equal to 75% oleic) and low polyunsaturated fatty acid content (linoleic and/or linolenic), displays good oxidative stability with acceptable low-temperature properties. This makes them well suited for use in greases compared to conventional vegetable oils [46].

In addition to the lubricating fluids, the toxicity and biodegradability of additive components is important. Over the years many of the additives that were originally based on fractions cut from petroleum- or coal-derived liquids are now synthetic and, therefore, are of much higher purity. Linear side hydrocarbon groups have in many instances replace branched and aromatic functional groups. This results in greater potential biodegradability. Toxicity of additives is related to metals in many cases. Current trends are to replace metal-containing additives with ashless varieties having similar or greater performance features. This will result in a lower pollutant load on the environment. Even military formulations are moving toward more environmentally friendly versions.

Environmentally friendly grease is used in applications such as agriculture, construction, forestry, marine, mining, and railroad. Specific applications include tramway tracks and railway switches, wheel flange lubricant for railways, and farm tractors.

11 SUMMARY

In summary, grease finds application where fluid lubricants may drip or leak from the point of application. Grease reduces the need to frequently lubricate a particular site, because the grease structure acts as a lubricant reservoir. Grease is very effective where lubricant is needed on a vertical machine component or at positions that are difficult to reach. Grease acts as a physical barrier that is effective in sealing out external contaminants and provides better protection when contaminated than does a liquid lubricant. Grease can also provide noise reduction in certain applications and is effective in protecting equipment at high temperatures and pressures and under conditions where there is shock loading in the lubricated components.

The formulation of grease can be considered an art and/or a science depending on the researcher questioned, but certain guidelines are generally useful.

For low-temperature applications, grease can use a low-viscosity, high-viscosity index (VI) lubricating fluid with a relatively low thickener content. The fluid lubricant should have a low pour point and good pumpability and rust protection. Grease for high-temperature applications will typically have a higher-viscosity lubricating fluid and high-temperature complex thickener. This will result in grease with a

higher dropping point. This type of grease will also find application where low flammability and, therefore, low volatility are design requirements.

Grease for applications where water contamination is an issue should be designed with a water-resistant thickener and generally a high-viscosity lubricating fluid. The grease should have low water washout and low water spray-off, which can be improved by incorporating a tackiness additive. Any application in a wet environment requires that the grease have excellent rust and corrosion protection. Careful formulation to balance the chemistries of the needed additives is critical in achieving the desired performance where surface protection is so important to machine life. Where shock or heavy loads are applied, grease is formulated using high-viscosity lubricating fluids and should include higher concentrations of anti-wear and extreme-pressure additives. This combination will provide both thicker lubricant film and appropriate additive chemistry to protect the metal surfaces.

Grease used in a centralized system needs to have a low to moderate thickener concentration and a relatively low-viscosity lubricating fluid so that the grease exhibits a lower apparent viscosity and can be readily pumped throughout the system.

12 EFFECTS OF INDIVIDUAL ADDITIVES AND GREASE SOAPS

This section includes a sample of application data where various grease additives were employed to modify the performance of various greases. The first section describes the use of individual additives with a particular type of grease. The second section demonstrates some synergistic effects of combining two or more additives that individually may not provide all the performance benefits needed.

An excellent general review of the fundamental characteristics of synthetic lubricating greases has been published [47]. This review describes the very wide range of potential synthetic greases in terms of properties and performance capabilities but also cautions that some of these higher-performance capabilities are not always needed and, thus, the higher cost of synthetics may not always be justified. Previously published chapters on greases can be found in earlier books [48,49].

These application data are meant to serve as a guideline, not as a recipe for greases. The actual combination of all the components of grease, including the base oil, thickener, each additive, and the order of addition, will affect the properties and performance of a final grease formulation, and thus these issues are left for the formulator. A list of additive components has also been included in [Table 6](#).

This data in [Table 7](#) show the results of wear experiments on aluminum complex grease using four organo-molybdenum-containing additives at the same concentration. Molyvan A is a powder, and any heterogeneity in the lubricant might result in the observed higher wear scars in grease made with this additive.

Comparison of aluminum complex and lithium complex grease with one level of Vanlube 829 showed improvement in both Four-Ball EP weld load and Four-Ball wear scar in the lithium complex grease ([Table 8](#)). It should be noted that the weld load difference in these results is within experimental error, but the combined improvement in weld load and wear scar is directionally desirable.

The data in [Table 9](#) show the improved performance of an aluminum complex grease containing Vanlube 622 over the grease containing a similar amount of Vanlube 73 or Vanlube 7723. There should be concern over the high sulfur content of

Table 6 Grease Additives—Chemical Components

Molyvan L: Molybdenum di (2-ethylhexyl) phosphorodithioate
Molyvan 822: Molybdenum dialkyldithiocarbamate in oil
Molyvan 855: Organo-molybdenum complex
Molyvan A: Molybdenum di- <i>n</i> -butyldithiocarbamate
Vanlube 829: 5,5-Dithiobis (1,3,4-thiadiazole-2(3H)-thione)
Vanlube 73: Antimony tris(dialkyldithiocarbamate) in oil
Vanlube 7723: Methylene bis(dibutyldithiocarbamate)
Vanlube 622: Antimony o,o-dialkylphosphorodithioate in oil
Vanlube 8610: Antimony dithiocarbamate/sulfurized olefin blend
Vanlube NA: Alkylated diphenylamines
Desilube 88: Blend of phosphate and thiosulfate
Irgalube 63: Ashless dithiophosphate
Irgalube TPPT: Triphenyl phosphorothionate
Lubrizol 1395: Zinc dialkyldithiophosphate (ZDDP)
Lubrizol 5235: Sulfur-phosphorus-zinc additive package
Lubrizol 5034A: Sulfur-phosphorus industrial gear oil additive package
Amine O: Substituted imidazoline
Sarkosyl O: N-oleyl sarcosine
Na-Sul ZS-HT: Zinc dinonylnaphthalene sulfonate/carboxylate complex
MoS ₂ : Molybdenum disulfide

Vanlube 622 and its effect on copper corrosion for applications where the grease will be in contact with copper-containing components.

Comparison of two antimony-containing EP/AW additives in aluminum complex grease showed improved EP performance and lower wear scar diameter for the sulfurized antimony dithiocarbamate (Vanlube 8610) (Table 10). Comparison of two sulfur-phosphorus EP additives in aluminum complex and lithium complex grease shows extremely high Four-Ball EP performance using Desilube 88 compared to Irgalube 63 (Table 11).

12.1 Food-Grade Greases

Food-grade greases are a special class of grease that requires nontoxic components approved for this particular application. Additional discussion and details can be found in Chapter 18 of this book.

Table 7 Organo-Molybdenum Compounds in Aluminum Complex Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Base grease (880 SUS paraffinic base oil blend)	—	126	0.68
Molyvan L	3.0	200	0.48
Molyvan 822	3.0	250	0.60
Molyvan 855	3.0	250	0.58
Molyvan A	3.0	250	0.76

Table 8 Thiadiazole Compound in Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Aluminum complex base grease (900 SUS paraffinic base oil blend)	—	140	0.59
Lithium complex base grease (600 SUS paraffinic base oil)	—	180	0.61
Vanlube 829 in aluminum complex	3.0	620	0.66
Vanlube 829 in lithium complex	3.0	800 kg pass	0.50

The data in [Table 12](#) demonstrate the better balance of EP and wear protection by the addition of calcium carbonate when compared to Desilube 88 alone. Rust protection is demonstrated by the synergistic effect of the two corrosion inhibitors using ASTM D 1743. The individual additives are not effective alone in providing sufficient EP and wear protection in this formulation.

12.2 Synergistic Additive Effects

Frequently, combinations of two or more additives show enhanced performance over that of the individual components. The occurrence and magnitude of synergistic behavior involving specific compounds very likely depend on the nature of the base grease, including the base oil and the thickener.

The use of Vanlube 829 in combination with Irgalube 63 showed improvement in the Four-Ball wear scar compared with Vanlube 829 in combination with Irgalube TPPT ([Table 13](#)). These combinations were each better in EP performance than formulations containing only Irgalube 63 or Irgalube TPPT in the absence of Vanlube 829. Desilube 88 and MoS₂ showed significant improvement in EP and wear performance for aluminum complex grease when compared to lithium complex grease ([Table 14](#)).

Table 9 Effect of Antimony Compounds in Aluminum Complex Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Aluminum complex base grease (880 SUS paraffinic base oil blend)	—	126	0.68
Vanlube 73	3.0	315	0.84
Vanlube 7723	3.0	315	0.81
Vanlube 622	3.0	500	0.46

Table 10 Antimony DTC and Antimony DTC/Sulfurized Olefin in Aluminum Complex Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Aluminum complex base grease (880 SUS paraffinic base oil blend)	—	126	0.68
Vanlube 73	3.0	315	0.84
Vanlube 8610	3.0	400	0.74

Table 11 Sulfur-Phosphorus Compounds in Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Aluminum complex base grease (900 SUS paraffinic base oil blend)	—	140	0.59
Lithium complex base grease (600 SUS paraffinic base oil blend)	—	180	0.61
Desilube 88 in aluminum complex	3.0	800	0.76
Desilube 88 in lithium complex	3.0	620	0.88
Irgalube 63 in aluminum complex	3.0	250	0.60
Irgalube 63 in lithium complex	3.0	315	0.55

Table 12 Food Grade Aluminum Complex Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)	Rust Test ASTM D1743
Aluminum complex base grease (550 SUS Technical White mineral oil)	—	140	0.62	Fail
Calcium Carbonate	4.0	315	0.49	—
Calcium Carbonate	4.0	315	0.55	Pass
Amine O	0.5			
Sarkosyl O	0.5			
Amine O	0.5	160	0.80	Pass
Sarkosyl O	0.5			
Desilube 88	3.0	500	1.04	—

Table 13 Synergistic Compounds in Aluminum Complex Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Aluminum complex base grease (880 SUS paraffinic base oil blend)	—	126	0.68
Vanlube 829	1.0	400	0.88
Irgalube TPPT	3.0		
Vanlube 829	1.0	400	0.60
Irgalube 63	3.0		
Irgalube 63	3.0	250	0.50
Irgalube TPPT	3.0	200	0.55

Table 14 Addition of MoS₂ in Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
MoS ₂ in lithium complex (600 SUS paraffinic base oil)	3.0	500	0.72
MoS ₂ in aluminum complex (900 SUS paraffinic base oil blend)	3.0	400	0.90
MoS ₂	1.3	500	1.0
Desilube 88 in lithium complex	3.0		
MoS ₂	1.3	800	0.8
Desilube 88 in aluminum complex	3.0		

Table 15 Effect of a Sulfonate Additive in Lithium 12-OH Stearate Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Vanlube 73	3.0	250	0.73
Vanlube 73	3.0	250	0.47
Na-Sul ZS-HT	1.0		

Table 16. ZDDP Component in Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Aluminum complex base grease (900 SUS paraffinic base oil blend)	—	140	0.59
Lithium complex base grease (600 SUS paraffinic base oil)	—	180	0.61
Lubrizol 1395 in lithium complex	3.0	315	0.47
Lubrizol 1395 in aluminum complex	3.0	250	0.55

Table 17 S-P-Zn-N Additive Package in Aluminum Complex Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Lubrizol 5235 in aluminum complex (900 SUS paraffinic base oil blend)	3.0	250	0.57
Lubrizol 5235 in lithium complex (600 SUS paraffinic base oil)	3.0	315	0.50

Table 18 Oxidation Stability in Organoclay Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)	Oxidation stability psi loss @ 500 h ASTM D 942
Organoclay base grease (600 SUS paraffinic base oil)	—	126	0.61	13.0
Molyvan A in organoclay	1.4	200	0.52	17.0
Molyvan A	1.4	200	—	12.0
Vanlube NA in organoclay	0.5			

Table 19 S-P Gear Oil Package in Grease

Additive	Wt. %	4-Ball EP weld load (kg)	4-Ball Wear scar diameter (mm)
Lubrizol 5034A in aluminum complex (900 SUS paraffinic oil blend)	3.0	250	0.45
Lubrizol 5034A in lithium complex (650 SUS paraffinic base oil)	3.0	315	0.50

A sulfonate rust inhibitor can enhance the Four-Ball wear performance of a lithium 12-hydroxy stearate grease in combination with an EP additive that by itself does not show reduced wear at low loads [50] (Table 15). A widely used antiwear additive, zinc dialkyldithiophosphate (ZDDP) exhibits moderate EP performance and low wear scars in both aluminum and lithium complex greases compared to the base greases alone (Table 16).

A multifunctional additive package specifically designed for greases provides good EP and AW performance. In general, this additive package also provides antioxidant and anticorrosion properties and copper metal deactivation (Table 17). EP additives can sometimes be detrimental to the oxidative stability of the grease. The addition of an amine antioxidant can improve the oxidation stability of EP-containing organoclay grease, as shown in Table 18.

Because gear oils can require good EP and antiwear properties, they are sometimes used in grease formulations. A sulfur-phosphorus industrial gear oil additive package exhibited good EP and wear performance in both aluminum complex and lithium complex greases (Table 19).

Note

Additional additives such as rust and corrosion inhibitors and antioxidants are usually added to the above examples to provide fully formulated grease. The Four-Ball EP test has a repeatability and reproducibility of one loading. The Four-Ball Wear test has a repeatability of 0.2-mm wear scar diameter and a reproducibility of 0.37 mm.

Acknowledgements

The authors would like to thank Henry Kruschwitz of Rhodia, Inc., for his help and the use of his laboratory.

REFERENCES

1. A Polishuk. Expanded graphite as a dispersed phase for greases. NLGI Spokesman 61(2):38, May 1997.
2. D Klamann. Lubricants and Related Products. Weinheim: Verlag Chemie, 1984, pp 177–217.

3. CJ Boner. Modern Lubricating Greases. New York: Scientific Publication Ltd., 1976.
4. The NLGI Grease Production Survey Report for the year 2000.
5. Lubrizol, Ready reference for grease. The Lubrizol Corp, Wickliffe, OH, Oct. 1999.
6. JA Brown, CN Hudson, LD Loring. Lithium grease-detailed study by electron microscope. The Institute Spokesman 15(11):8–17, 1952.
7. ASTM D-217. Standard test methods for cone penetration of lubricating grease. Annual Book of ASTM Standards, Philadelphia, Sec 5, Vol 5.01, 1996.
8. Technology of modern greases. Lubrication (Texaco Inc., New York) 77(1). 1991.
9. AC Witte. DA Turner. Grease making in the 90's. NLGI Spokesman 58(3):97–107, June 1994.
10. Continuous grease manufacture. Lubrication (Texaco Inc., New York) 55(1), 1969.
11. T. Okaniwa, H. Kimura. NLGI Spokesman 61(3):18–24, 1997.
12. PA Bassette. Presented at the 1997 Annual Meeting on the NLGI, Carlsbad, CA, October 26–29.
13. Grease. In JG Wills, Lubrication Fundamentals. New York: Marcel Dekker, 1980, pp 59–74.
14. ASTM D 1403. Standard test methods for cone penetration of lubricating grease using one-quarter and one-half scale cone equipment. Annual Book of ASTM Standards, Philadelphia, Sec 5, Vol 5.01, 1996.
15. ASTM D 2265. Standard test method for dropping point of a lubricating grease over wide temperature range. Annual Book of ASTM Standards, Philadelphia, Sec 5, Vol 5.01, 1996.
16. Grease—The world's first lubricant. NLGI Spokesman, 59(5):1–8, insert, August 1995.
17. AT Polishuk. Properties and performance characteristics of some modern lubrication greases. Lubr Eng 33(3): 133–138, March 1997.
18. M Hermansson, E Johansson, M Jansson. J. Synthetic Lubr 13(3):279–288, 1996.
19. ASTM D 2266. Standard test method for wear preventative characteristics of lubricating grease (four-ball method). Annual Book of ASTM Standards, Philadelphia, Sec 5, Vol 5.01, 1996.
20. ASTM D 2596. Standard test method for measurement of extreme-pressure properties of lubricating grease (four-ball method). Annual Book of ASTM Standards, Philadelphia, Sec 5, Vol 5.01. 1996.
21. NLGI Lubricating Grease Guide, 4th Ed., 1996.
22. G Fagan. Complex soap greases. Presented at NGLI 64th Annual Meeting, Carlsbad, CA, 1997.
23. RL Frye. An introduction to lubricating greases. Presented at NLGI 64th Annual Meeting, Carlsbad, CA, 1997.
24. CJ Boner. Manufacture and Application of Lubricating Greases. New York: Reinhold Publishing Corp, 1954.
25. BW Hotten. *Advances in Petroleum Chemistry and Refining*, Vol. 9. New York: Interscience Publishers, 1964, Chapter 3.
26. JW Wilson. Three-dimensional structure of grease thickener particles. NLGI Spokesman 3:372–379, 1994.
27. G Arbocus. When greases don't perform. Lubricant's World 3(10):7–8, Oct 1993.
28. R Czarny. Effect of changes in grease structure on sliding friction. Industrial Lubr and Trib 47(1):3–7, 1995.
29. S Hurley, PM Cann, HA Spikes. Trib Trans 43(1):9–14, 2000.
30. JA Williams. Engineering Tribology. New York: Oxford University Press, 1994.
31. ER Booser, ed. CRC Handbook of Lubrication, Vol. 2. Boca Raton, FL: CRC Press, 1984.
32. J Pemberton, A Cameron. A mechanism of fluid replenishment in elastohydrodynamic contacts. Wear 37:185–190, 1976.

33. Boundary Lubrication (Texaco Inc.) 57(1), 1971.
34. DD Fuller. Theory and Practice of Lubrication for Engineers. New York: John Wiley, 1984.
35. Encyclopedia for the User of Petroleum Products. Lubetext DG-400, Exxon Corp, 1993, p 10.
36. O Rohr. NLGI Spokesman 61(6):10-7, 1997.
37. O Rohr. Presented at NLGI 63rd Annual Meeting, Scottsdale, AZ, Oct 27–30, 1996.
38. JP King. Presented at 1998 NLGI Annual Grease Meeting, Dublin, Ireland.
39. YL Ischuk et al. NLGI Spokesman 61(6):24–30, 1997.
40. T Ogawa et al. Presented at NLGI 64th Annual Meeting, Carlsbad, CA Oct 21–29, 1997.
41. L Tocci. Transparent grease bears a heavy load. Lubes-n-Greases 3:52–54, April 1997.
42. T Ogawa, H Kimura, M Hayama. NLGI Spokesman, 62(6):28–36, 1998.
43. K Seki, M Nishimura. J Synthetic Lubrication 9(1):17–27, 1992.
44. RJ Lewis Sr. Hawley's Condensed Chemical Dictionary, 13th New York: Van Nostrand Rheinhold, 1997, p 977.
45. I-S Rhee. NLGI Spokesman 63(1):8–18, 1999.
46. S Lawate, K Lal, C Huang. In ER Booser, ed. Tribology Data Handbook. Boca Raton, FL: CRC Press, 1997, pp 103–116.
47. PS Coffin. J Synthetic Lubr (1):34–60, 1984.
48. P Bassette, RS Stone. In LR Rudnick, RL Shubkin, eds. Synthetic Lubricants and High-Performance Functional Fluids. New York: Marcel Dekker, 1999, pp 519–538.
49. RC Schrama. In ER Booser, ed. Tribology Data Handbook. Boca Raton, FL: CRC Press, 1997, pp 138–155.
50. RF Baker, PF Vaast, Jr. NLGI Spokesman 55(12):23-487–25-489, March 1992.

PART III

TRENDS

Long-Term Trends in Crankcase Additives: Lubrication for the Future

SHIRLEY E. SCHWARTZ

General Motors Powertrain, Warren, Michigan, U.S.A.

STELLA PAPASAVVA

*Research and Development and Planning Center, General Motors,
Warren, Michigan, U.S.A.*

LESLIE R. RUDNICK

*The Energy Institute, The Pennsylvania State University, University Park,
Pennsylvania, U.S.A.*

1 HISTORICAL OVERVIEW

A lubrication issue of several thousand years ago was probably: “What’s the best kind of lubricant to use to help us pull large stones from the quarry to the site where we wish to build a pyramid?” Egyptian art suggests that oil poured on the rubbing surfaces helped facilitate friction reduction.

During the era of emergence of mathematical analysis, one might have heard the concern: “Do you think we’ll ever be able to create mathematical equations to describe fluid flow in a lubricated contact?” The success of the Reynolds equation and other mathematical descriptions of lubrication effects provided proof that the field of mathematics could be successfully applied to empirical knowledge in the field of lubrication.

During the age of proliferation of machinery, economic pressures required manufacturers to increase the useful life of their machines. These economic pressures promoted the search for chemical agents to prolong the life of the lubricant and provide corrosion and wear protection to the hardware. In addition, these efforts

resulted in specialization that adapted a lubricant to the needs of the specific hardware in which the lubricant was used. One such adaptation is seen in automotive engine lubrication. Engine oil at the dawn of the automotive era was not highly specialized or standardized, and exceedingly frequent oil changes were required.

Over a period of many years, oil additives were identified that solved a variety of engine problems: corrosion inhibition, ability to keep particles such as soot dispersed, ability to prohibit acidic combustion products from plating out as varnish on engine surfaces, and ability to minimize wear by laying down a chemical film on heavily loaded surfaces. Test methods were developed to ensure that engine oil provided protection in all of these areas. In addition, engine oil became specialized so that requirements for diesel engine oils began to diverge from requirements for gasoline engines, since enhanced dispersive capability was needed to keep soot from clumping in the oil of diesel engines.

Standard test methods were developed, and licensing procedures were put in place so that an educated driver could identify whether a given engine oil had passed the standard tests. Mathematical techniques were developed to predict fluid-film thickness and fluid temperatures in heavily loaded contacts, so that designers could adapt their hardware to minimize field problems.

These examples highlight the fact that lubrication technology has been enhanced by the incorporation of concepts from a variety of technical disciplines: models for fluid flow (from the domain of mathematics and mechanical engineering), oil additives to provide chemical stability and corrosion and wear protection (chemistry), viscosity modifiers to maintain viscosity stability (polymer science), and biocides to provide resistance to microbial attack (biology). This trend toward incorporation of wisdom from a variety of technical disciplines is sure to continue and expand.

2 CHARACTERISTICS OF CRANKCASE LUBRICANTS

A typical automotive crankcase lubricant consists of oil (base stock) and additives. The base stock may be categorized in several different ways. For example, the base stock may be composed of petroleum that has come out of the ground and that has been distilled or separated into a desirable molecular-weight fraction for use in engine oil. This fraction may be further enhanced by such processes as extraction, dewaxing, or chemical reaction to remove undesirable constituents. Such base stocks are typically called “mineral” oils.

If the base stock is formed by combining low-molecular-weight building blocks, it is typically designated as “synthetic.” Some mineral base stocks that have been severely hydrotreated to remove double bonds and undesirable chemical contaminants may also be considered as synthetic. Synthetic base stocks tend to be more resistant to chemical and thermal degradation than “mineral” base stocks. In addition, engine oil base stocks may consist of any mixture of synthetic and mineral base stocks.

An example of the difference in the rate of oxidation of a synthetic engine oil compared to the degradation rate of a mineral oil is shown in [Figure 1](#) for engine oils in freeway service [1]. “DSC” represents oxidation induction time in terms of minutes, as determined by differential scanning calorimetry. $\ln(\text{DSC})$ represents the natural logarithm of the oxidation induction time. The DSC test was conducted

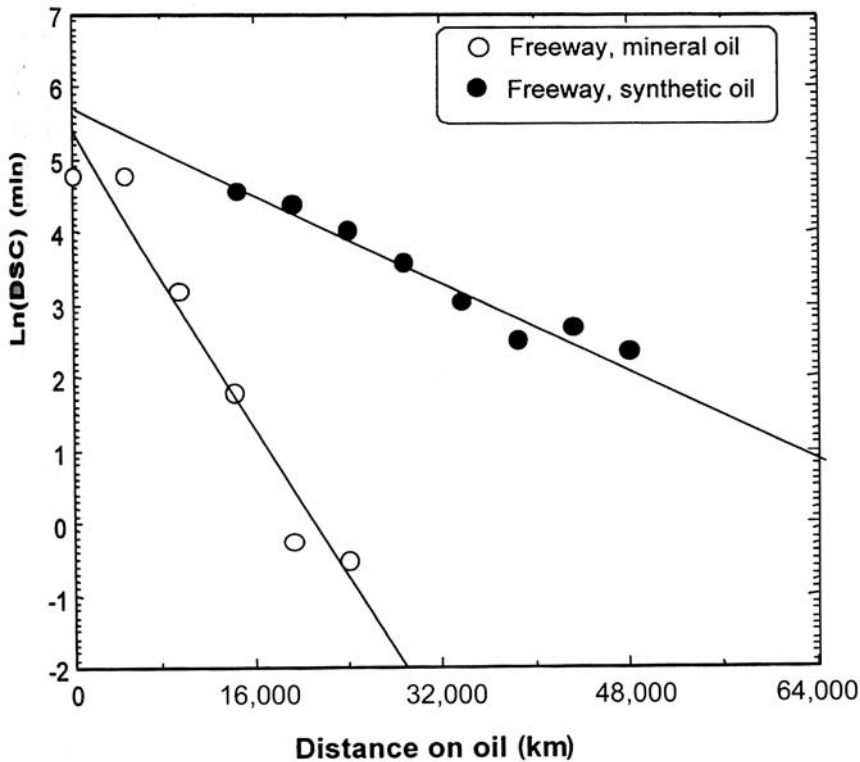


Figure 1 Differences in the rate of loss of antioxidant protection, mineral oil compared to synthetic oil, freeway driving, 5.7L engine.

by placing a drop of used oil in an oxygen atmosphere (3800 kPa oxygen pressure at 175°C, per American Society for Testing and Materials test method ASTM D 6186) and noting the time required before rapid oxidation occurred. The rate of oxidation of the synthetic oil (solid circles) was slower than that of the mineral oil (open circles).

To create a suitable engine oil, additives are blended into the base stock. The additives either enhance the stability of the lubricant or provide additional protection to the engine. The presence of additives in the oil is necessary, otherwise the oil could not pass the severe standard tests required before the oil can display the label indicating that the oil meets current specifications.

Engine oil additives include such products as antioxidants, antiwear agents, detergents, dispersants, viscosity index improvers, defoamers, and pour point depressants. Antioxidants ensure that the lubricant base stock (that is, the oil) resists breakdown from exposure to heat and oxygen from the air. Both the composition of the base stock and the nature of the antioxidants in the oil formulation influence the rate of oil oxidation. Some types of antioxidant also serve as an antiwear agent by laying down a protective chemical film on a rubbing iron surface. The chemical film provides boundary lubrication that protects iron in the engine against wear in heavily loaded contacts.

Alkaline agents (detergents) neutralize organic acids that form when oil is exposed to hot spots in the engine, in the presence of oxygen. Thus, detergents keep acids from plating out on engine surfaces, which helps keep the surfaces clean. Dispersants keep contaminants (such as oil degradation products or products from the partial combustion of fuel) from clumping and possibly blocking critical flow passages. Viscosity index improvers help reduce viscosity variability despite temperature fluctuation. Defoamers are surface-active agents that reduce surface tension and allow air bubbles to escape from the oil's surface. The air bubbles are typically generated as a consequence of the oil turbulence that occurs during heavy accelerations.

3 CURRENT CONCERNS

Current crankcase lubrication issues focus to a considerable extent on several topics:

- Upgrading standard test methods for crankcase lubricants, to enhance engine durability
- Attempts to develop worldwide standard test methods for qualification of passenger car lubricants so that a lubricant manufacturer will not have to pass related (but not identical) tests on three different continents
- Incorporating low-friction oil additives and engine materials to promote energy efficiency and reduce fuel consumption
- Life-cycle assessment to help determine the true costs and tradeoffs for any modifications proposed for oils or engines
- Pollution control during use and disposal to reduce environmental contamination

Tradeoffs between the cost and quality of both the oil and the engine require both vehicle and lubricant manufacturers to make difficult decisions.

Priorities for future development are typically related to the industrial field in which an individual investigator works. For example, specific questions that an additive manufacturer or a crankcase lubricant supplier might wish to address include:

- Can engine oil become more environmentally friendly?
- Will it be possible to reduce the concentration of (or eliminate) components from the oil's additive package (for example, phosphorus-containing products) that are of concern with regard to environmental issues, but still provide adequate wear protection to the engine?
- Can energy efficiency of the oil or additives be increased without creating engine durability, safety, or environmental problems?
- Can the useful life of the oil be increased without compromising the durability, emissions control, or fuel efficiency of the engine?
- Is the entire life cycle of the engine oil and its additives understood (raw materials, processes during manufacturing, degradation during use, recycling options, and consequences of ultimate disposal), so that useful oil life is prolonged and disposal problems are minimized?
- To what extent can sustainable lubricating products be developed, so that there will not be an issue of dwindling or unavailable raw materials for future lubricants?

- If we think in terms of sustainability that endures “forever,” what should the composition of the lubricant and additive package be?

A vehicle manufacturer might be interested in issues such as:

- To what extent can alternative power sources (other than current internal combustion engines) be used?
- If alternative power sources are used, can they be made as reliable, safe, and cost-effective as current internal combustion engines?
- To what extent can friction be reduced by intelligent selection of engine design and materials, without compromising long-term engine durability and performance?
- If alternative materials are used in an engine or drivetrain to reduce mass and energy consumption, what modifications to the lubricant are needed to ensure that components are adequately lubricated?
- If surface coatings are used to reduce friction, will they last for the life of the engine, will they inhibit the formation of necessary lubricant films, or will they form unacceptable wear debris during use?
- If phosphorus and sulfur are reduced in concentration or removed from oil, will engine wear rates become unacceptable?
- Can an engine be modified such that very little engine oil is needed, but the engine is still protected?
- If we think in terms of “forever,” what will be required to meet the lubrication needs of a vehicle and also meet the mobility desires of the public?

Within each of these questions we can identify subcategories. For example, with regard to engine durability, standard test methods for qualifying oils for use in the crankcase are upgraded periodically to adapt to changes that have evolved in engines, fuels, and oils. Development of these standard methods and proving their reliability are slow and expensive processes. Thus, a relevant issue for engine, additive, and lubricant manufacturers is cost-effectiveness, because a manufacturer who does not make a profit is not likely to stay in business.

A current issue relative to reliability and cost-effectiveness is the fact that standard oil qualification tests in Japan, Europe, and North America are not identical. Thus, to qualify an oil for use in these three geographical regions (all of which have substantial automotive production and design capability), a lubricant manufacturer must pass three different sets of tests, representing the requirements of the three different geographical regions. It would be beneficial to have one set of standard tests that could be used worldwide. However, resolving this test-method issue is not a simple matter, since engines manufactured in the different geographical regions are not identical. There may be differences in engine materials, operating temperatures, typical loads, engine designs, driving styles, and driver preferences. Thus, a concern is that if a standard test method for engine oil is developed using an engine from one geographic location, the test might not adequately identify potential problems that might occur with a different engine designed to meet different driving conditions in its own geographical area. Active debate is ongoing regarding how to create acceptable, international test methods, but at the same time ensure that one engine type will not be adversely affected if a different engine design is used in the engine oil-qualification process. It may be possible to identify simplified bench tests to help

resolve some of these concerns, as was the case recently when the Ball Rust Test (developed by the Ethyl Corporation and General Motors) replaced the Sequence IID engine dynamometer test for evaluation of an oil's ability to provide rust and corrosion protection.

When considering an extremely long-range timeframe, a desirable direction for sustainable development is to approach a steady state, if possible, such that lubricants and engine hardware are derived from renewable sources, and all used products are recycled. Even though some engine oil is recycled, and recycling of engine materials is increasing, these efforts have not yet reached a state that could be considered completely sustainable. Major changes in design and performance will be required before sustainability can be achieved.

4 ALTERNATIVE POWER SOURCES

Various agents have been (or could be) used to power vehicles: gasoline, gasoline/alcohol blends (with ethanol or methanol), compressed natural gas, electricity, solar power, hydrogen, fuel cells, human-powered bicycles, and animal power. In addition, power generated from wind, wave, tide, and waterfalls has been converted to electricity, which can then be used to power vehicles. Each power source has its own advantages and disadvantages. A current challenge is to identify those alternative sources of power that have a chance of becoming commercially viable. One must then find ways to make them safe, efficient, and environmentally friendly.

Competitions such as solar challenge races (cross-country race for light-weight, low-friction, aerodynamically designed vehicles that run completely on solar power) encourage creativity and innovation with regard to design and energy efficiency. In addition, media hype associated with such events promotes awareness of the capabilities of alternative-fueled vehicles to the general public. However, such vehicles, on exposure to a cloudy day, would have to revert to some other power source under real-world conditions.

Subsidies for alcohol-fuel vehicles by states or agencies interested in promoting alternative fuels provide incentives for manufacturers and vehicle owners. However, it is exceedingly difficult to displace a current product (that is, trucks and passenger cars that run on diesel fuel or gasoline), because conventional fuels and engines have been overwhelmingly successful for current cars and trucks. Studies in the past have indicated that high-quality engine oils can be developed for alcohol-fueled vehicles. But, alcohol-fuel prices have typically been higher than those of petroleum-based fuels, and in addition, it is necessary to ensure that all engine materials (especially seals) are compatible with the target fuel. Additional areas of special concern, when considering the use of an alternative fuel, are toxicity and safety, which need to be addressed when considering such fuels as methanol or hydrogen.

Electric vehicles have been produced that have excellent acceleration and driving characteristics and very low noise levels. Disadvantages are that these vehicles may be heavy, may have limited range, and may need to have space taken from the passenger compartment for housing the batteries.

Each of the mobility options described in this section may require different lubrication techniques. For example, any lubricants used in electric vehicles will not have to face exposure to the exceedingly harsh conditions generated by the

by-products of combustion in an internal combustion engine. Thus, additives containing sulfur and phosphorus may not be needed.

5 OIL PROPERTIES

The properties of engine oil change during use, as a function of one or more of the following: degradation, contamination, or evaporation. *Degradation* is associated with a reduction in the effectiveness of the oil's additives as a consequence of exposure to hot spots or chemical reaction with contaminants. *Contamination* of engine oil occurs when dust or chemical pollutants enter the crankcase from the atmosphere. Additional mechanisms for introducing contaminants into the engine oil include condensation of fuel or fuel reaction products, leaching of materials out of seals or other engine components, accumulation of debris that originated from metal or elastomeric materials in an engine, coolant leaks, or oil degradation products. *Evaporation* of the oil can occur when the oil is exposed to hot spots in the engine.

An example of oil degradation is shown in Figure 2. Acids are formed via partial combustion of the fuel or by oxidation of the oil in hot spots. Engine oils are intentionally made alkaline so that they can resist this corrosive (acidic) attack from oxidized fuel or from the hot spots in the engine. The strength of the reserve alkalinity in the oil (sometimes designated TBN, for total base number) provides an assessment of the extent to which the engine oil has degraded during service as a consequence of acidic attack. In a TBN test the oil's alkaline corrosion inhibitor (as measured by ASTM D 2896 or other base number test) is titrated against a standard acid, and the amount of acid required to neutralize the oil is determined. As long as the oil remains alkaline, engine corrosion is less likely to occur.

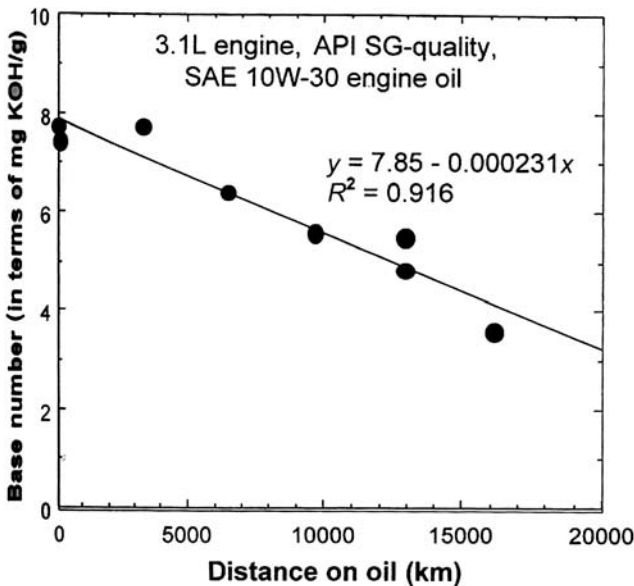


Figure 2 Rate of loss of engine oil alkalinity, freeway driving.

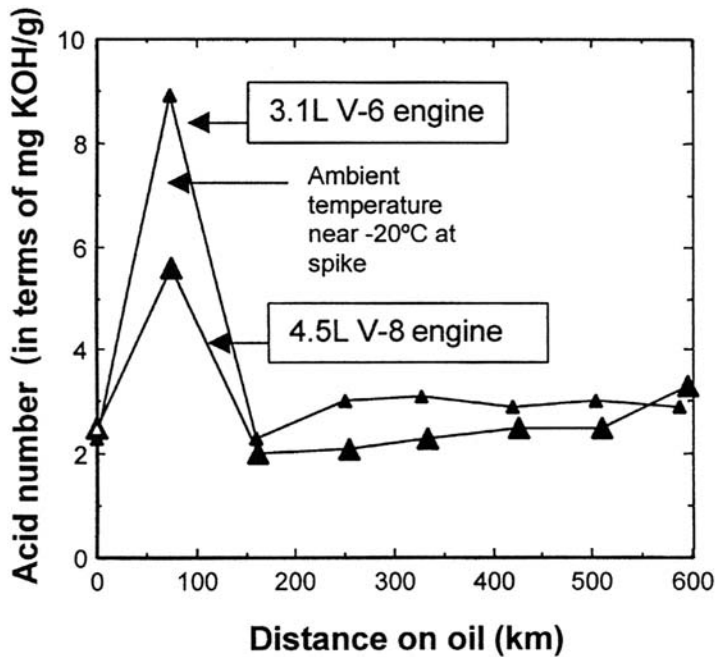


Figure 3 Spike of acidity due to condensation of volatile combustion products in engine oil during exceedingly low-temperature, short-trip service (3 km/trip, 3 trip/day, 5 days/week), and removal of acids once ambient temperature increased.

Figure 3 indicates that acids (from partially combusted fuel during starts at very low temperature) can condense directly in the engine oil [2]. These fuel combustion products evaporate from the engine oil once the weather warms or the engine oil sump reaches normal operating temperature, but such condensed contaminants are potential sources of engine corrosion while they remain in the oil or in the air space above the oil.

Organic acids can also be formed via oxidation of the engine oil in engine hot spots. Once these acids have formed, they can cause engine oil to thicken or gel, particularly once the engine has been shut off and the oil is allowed to cool under winter (low-temperature) conditions. Antioxidants inhibit the formation of these organic acids.

Viscosity of the engine oil does not remain constant during use. Cold oil is much more viscous than hot oil. Viscosity can be significantly reduced, at a given oil temperature, if fuel has entered the oil during a sequence of many short trips in winter. An extreme example of this low-temperature viscosity change caused by fuel entering the oil is shown in Figure 4 [2]. In this figure there is approximately a 60% reduction in the 40°C oil viscosity. Because the oil did not warm completely, the low-temperature thickening of the oil compensates somewhat for the thinning effect of fuel in the oil.

During high-temperature driving—for example, pulling a trailer or climbing a mountain—oil viscosity can increase as a consequence of evaporation of the lighter ends of the oil (in addition to the thickening effect of oil degradation products).

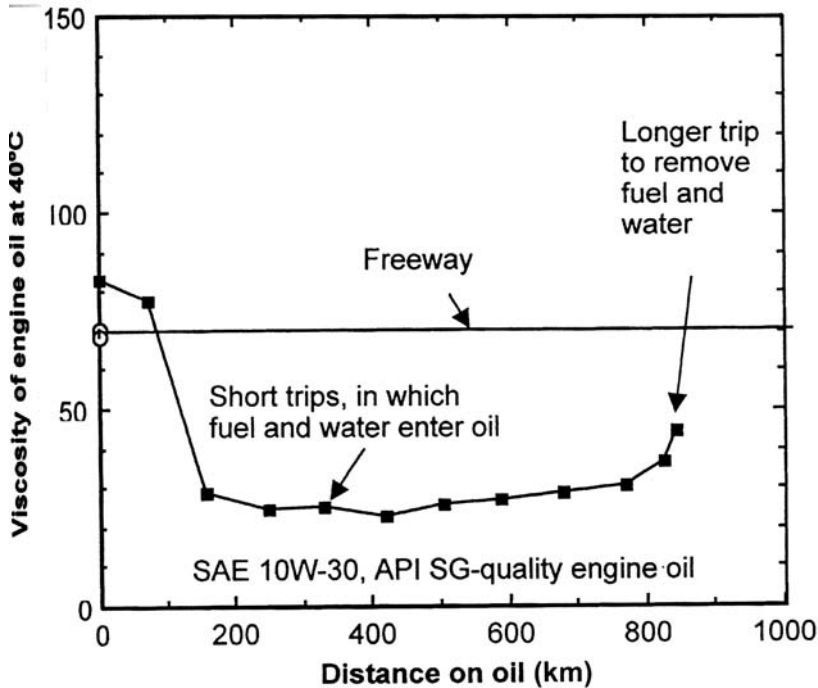


Figure 4 Effect of short trips and fuel in engine oil on oil's viscosity.

Evaporation of the lighter ends of the engine oil is most likely to occur in the engine's hot spots. A scenario for this effect is approximately as follows. Oil flows over a hot spot. The lighter ends of the oil evaporate, leaving an oil base stock that has lost a slight amount of its lowest molecular-weight components. This higher-viscosity portion of oil is then mixed into the bulk of the engine oil. Thus, the average molecular weight of the bulk of the oil has now increased slightly. When this process has been repeated many times, the engine oil viscosity becomes measurably higher.

A synthetic oil is less likely to exhibit this evaporative thickening effect at high oil temperatures, since a synthetic oil typically has a narrower range of base stock molecular weights than a mineral oil. Thus, fewer low-molecular-weight oil molecules are available to evaporate from a synthetic oil.

In addition to evaporative thickening, gelation can also occur under the following set of circumstances. Mineral oil typically has more double bonds between carbon atoms than are found in synthetic oil base stocks. The double bonds are more susceptible to oxidation than is typically found with single bonds. If oxygen (or nitrogen) attacks a double bond, a polar compound (such as an acid or aldehyde or ketone) is formed, if used engine oil (which has aged past the point of a normal oil change) becomes cold (for example, parked in below-freezing winter conditions), the engine oil can gel (that is, the oil can become highly resistant to flow).

A related effect can occur at high temperatures. Oxidized oil can plate out on hot surfaces to form a varnish. Since very high temperatures are found in the combustion chamber or on the piston, these are likely sites for such deposit formation to occur.

Many oils contain viscosity index improvers (sometimes abbreviated “VII”) that provide multigrade viscosity characteristics such as 10W-40 or 5W-30 viscosities (that is, the viscosity index improver makes the oil a little thicker when the oil is hot and has minimal impact when the oil is cold). Some viscosity index improvers shear during operation, which means the oil loses some of its multigrade characteristics. As a consequence, there may be a slight loss of viscosity (perhaps in the range of 10%) at normal operating temperatures for some oils. However, viscosity reduction due to increased oil temperature (for example, during hill climbing or heavy accelerations) or the effect of fuel in the oil during short trips (as shown in [Figure 4](#)) is likely to reduce viscosity to a greater extent than is typically observed as a consequence of the shear loss effect in current engine oils.

6 EXTENDING OIL-DRAIN INTERVALS

Many vehicle manufacturers recommend that engine oil should be changed in the range of 5000 km (3000 miles) or 3 month if trips are short, and in the range of 10,000 to 12,000 km (or 7500 miles) or 1 year if trips are long and driving conditions are mild. Studies of driving habits of the general population indicate that a significant proportion of vehicle trips (engine on to engine off) are in the short-trip category (trips shorter than 15 km). Some of these short-trip drivers do not realize that short trips are considered severe service. In order to ensure that engine oil will be changed at the right time, some vehicle manufacturers are now starting to use sensors or models of oil life to determine the oil-change point and to provide notification to the driver to change oil.

Sensors are available that measure such oil characteristics as viscosity, acidity, and presence of polar contaminants [5–9]. On-board computer models of oil life calculate the rate of oil degradation and include compensation for those driving conditions that cause the engine oil to degrade at a faster rate than would occur during easy freeway driving [10,11]. For example, in the oil life model of Schwartz and Smolenski [11], such oil characteristics as remaining antioxidant protection, relationship between oil acidity and alkalinity, and accumulation of insoluble material in the oil provided guidelines regarding whether the oil’s additives have degraded to an unacceptable extent. “Unacceptable extent” typically varies with the requirements of a given set of test conditions and the judgment of the investigator. Typical “unacceptable” oil analysis values may vary by a factor of 5 for a given driving test, a given version of an oil analysis test, and a given investigator, as described in [12].

For a few drivers (for example, short-trip drivers in a winter climate), a “change oil” signal from an on-board oil-monitoring device may turn on sooner than the driver expects (perhaps at 5000 km or less). And the driver, not necessarily realizing he was driving under “severe service” conditions, will be surprised. However, on-board models of oil life or oil conditions sensors typically have been carefully crafted, using data of the type shown in [Figures 1, 2 and 3](#), to ensure that oil is changed before engine damage is likely to occur. Some oil life models are incorporated into “service indicator” packages that include additional types of service warnings.

For many drivers who spend a considerable amount of time on the freeway and whose vehicle is equipped with an oil-change indicator, oil-change intervals may be increased beyond the 12,500-km distance that many North American owners manuals have recommended in the past. For example, some change intervals will reach

15,000 km to 30,000 km in some 2000 model-year vehicles. The drivers of these vehicles will, therefore, save time and money, and oil reserves will not be diminished as fast as would otherwise be the case. Some vehicle manufacturers who require the use of long-life engine oil can extend oil-drain intervals considerably beyond the distances that are recommend for less stable engine oils, as shown in [Figure 1](#).

7 ENVIRONMENT

Lubricant and hardware manufacturers are becoming aware that it is undesirable to allow their worn-out products to accumulate in the environment. Any time a product can be used, regenerated, and reused, the strain on landfills and the threat of major shortages will be diminished.

Many of the current issues that fall under the heading “environmental concerns” also overlap other general categories. For example, if engines are made lighter to reduce energy consumption, care must be taken to ensure that engine durability and occupant safety are not compromised. If sulfur is removed from fuel, and the concentration of sulfur and phosphorus is reduced in engine oil, vehicle manufacturers and engine oil producers must find ways to ensure that engine wear will not increase (since sulfur and phosphorus play a significant role in wear protection). If engine oil-change intervals are increased (to reduce the expense to the vehicle owner and to reduce the amount of oil that enters the environment), vehicle manufacturers must be certain that engine components will not be at risk.

Sometimes other substances also provide cause for concern. For example, Molybdenum and barium compounds have been used in engine oil formulations. However, there may be a concern regarding their health or environmental effects. Thus, there may be interest in removing them from such materials as engine oil. On the other hand, barium (in the form of barium sulfate) is used in medical diagnostic procedures, because barium sulfate is so insoluble in water that it poses essentially no health risk. Thus, the chemical state of a product must also be evaluated when a supplier has to decide whether or not to use a particular chemical in a lubricant formulation.

These are difficult issues to address, and finding suitable answers to the uncertainties requires considerable expense and time.

7.1 Recyclability

A major environmental issue is recyclability. Recycling waste engine oil is a desirable way to prolong the usable life of the oil. However, if waste engine oil is recycled and used in the formulation of fresh engine oils, the oil's quality must meet the same standards required of all certified engine oils. That is, engine oil must meet exceedingly strict requirements before it receives certification for use in vehicles. The required tests for this certification are time-consuming and expensive, but these tests ensure that the oil has suitable characteristics and appropriate additives to protect the engine. In addition, if engine-oil-change intervals are increased (which is desirable with regard to oil conservation), vehicle manufacturers must be certain that engine components will not be at risk.

Recently, recycled oils that meet standard test requirements for engine oils (or for other applications such as industrial lubricants) are becoming available. These

oils have been rerefined (that is, oil degradation products, spent oil additives, wear debris, and corrosion products from the engine have all been removed), so that what remains is equivalent to virgin oil that can be formulated into high-quality engine oil. Some commercial oil-change establishments are already collecting and sending used oil to be recycled. If vehicle owners who change their own engine oil are also encouraged to turn their used oil into a recycling collection point, this should permit the oil to be purified. Appropriate additives can then be incorporated. Thus, the oil will be reused, possibly for some other function such as industrial lubrication, where the requirements are not so strict or so costly as those for engine oil. However, some engine oil formulators are already capable of creating engine oils that pass the current standard tests, using rerefined oil as a starting point.

Any time a product can be used, regenerated, and reused, the strain on the environment should be diminished.

7.2 Removal of Sulfur and Phosphorus from Engine Oil

One issue receiving increased attention is the release of sulfur into the environment, as a consequence of burning sulfur-containing fuel. Sulfur is also an important ingredient in the detergent and in the antioxidant/antiwear agent in typical engine oils. During the combustion process a small amount of engine oil (at the top of the cylinder or in the form of oil mist) is at risk of being burned. Thus, some emissions control advocates are questioning whether there might be a benefit to reducing the sulfur content of engine oil. However, if the concentration of protective sulfur-containing components of engine oil is reduced, oil in hot spots in the engine will almost certainly be more susceptible to oxidative attack, which causes the formation of organic acids, varnish, and engine deposits. Thus, if sulfur is removed from engine oil, alternative chemical agents will need to be identified to perform the beneficial antioxidant function that sulfur compounds currently provide.

In addition to providing resistance to oxidation, some sulfur compounds can act as antiwear agents by forming a protective sulfur-containing film on iron surfaces in rubbing contacts. If sulfur must be reduced in concentration or removed from the oil, a significant effort will be required to identify alternative antiwear agents that do not contain sulfur. It is not certain whether it will be possible to create low-sulfur oil formulations that are as effective antiwear agents as current sulfur-containing formulations.

An issue of particular concern is the effect of sulfur and phosphorus on the catalyst [13,14]. Because the catalyst's function is to promote more complete combustion of the fuel, anything that upsets the efficiency of the catalyst is likely to cause environmental deterioration. Since sulfur and phosphorus poison the catalyst, efforts at finding alternative chemical agents that provide equivalent engine protection (antiwear, antioxidant, and corrosion inhibition) are of major importance for both the life of the engine and the preservation of the environment.

8 LONG-RANGE CONCERNS

Previous sections have focused on engine lubrication issues currently receiving considerable attention. However, one must also be able to visualize those areas certain to become major issues in the future. If the visualization process is sufficiently timely

and comprehensive, plans can be created and implemented to minimize the adverse consequences of any required changes.

The visualization process includes thoroughly assessing the current state of affairs, identifying those areas in which problems are anticipated, compiling a list of candidate tactics that may be beneficial in addressing the concerns, evaluating (insofar as possible) the benefits and disadvantages of the candidate tactics, and deciding which approaches should be implemented. Once such a procedure has begun, it must be evaluated periodically to ensure that newly gained knowledge continues to be incorporated into the plans for action. And if conditions have changed significantly, a new plan of action must be created.

The following section describes a process that is exceedingly beneficial in visualizing and assessing environmental, economic, and social impacts of a given technical development.

9 LIFE-CYCLE ANALYSIS

A technical discipline receiving increasing attention is “life-cycle analysis” [15]. This analysis addresses issues related to

- Sources from which components and end products are derived
- Environmental concerns associated with the collection and processing of the raw materials
- Conversion of raw materials into a desired end product
- Ways in which products are used in their normal lifetime
- Means of disposal
- Effects of disposal on the environment
- Extent to which products can be recycled
- Total cost of these steps, in terms of energy dissipated, amount of waste generated, money spent, environmental impact, and effort required.

Life-cycle analysis is becoming widely utilized by industry [16,17] and government to assess the total impact of a given technology, including generation of raw materials, manufacturing, use, and end of life effects. One goal of such an analysis is to identify the sources that contribute significantly to adverse environmental pollution and to provide design and manufacturing engineers the necessary information that allows them to choose among alternative technologies and procedures [18].

Life-cycle analysis is based on industrial ecology principles [19], taking into account that all energy and materials flow throughout the production, use, and end of life of a product. An industrial system is defined as any collection of operations that, when acting together, perform some defined function. [Figure 5](#) shows a schematic diagram of a system (inner box). This inner box represents the system boundary that separates the system from the system environment.

There is no restriction on the type of system that may be defined in this way. In the industrial sphere, systems may be simple production processes (designated “gate to gate”) or they may be increasingly extensive, ranging from ecological profiles (cradle to gate) or complete life cycles (cradle to grave). The factor that differentiates these differing types of systems is the nature of the inputs and outputs. For example, a simple production process will usually take in materials that have already been processed, and further processing will take place.

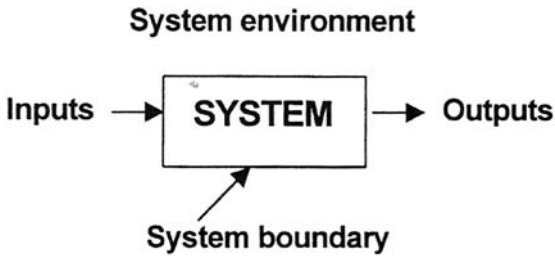


Figure 5 Simple schematic diagram of a system.

An ecological profile will start with raw materials in the earth and will follow all processing operations up to the production of some product at the factory gate ready for dispatch to another plant for further processing. A true life-cycle analysis starts with raw materials in the earth, follows all processing use, and disposal operations, and continues to the point that the only output is waste returned to the earth.

Life-cycle thinking provides a technique that allows the business world to be defined not as a world of unlimited resources, but as a world that puts values on items used in or influenced by industrial processes, including air, water, and the Earth's minerals and natural resources. Life-cycle thinking documents the interactions of matter and energy and assesses the consequences of those interactions [20]. It attempts to put a monetary value on raw materials, the processes required to convert the raw material to products, and the matter and energy involved in waste generation and removal. Thus, the traditional view (in which the energy and environmental impact of a given process are largely ignored) is now modified to calculate the environmental and financial cost of a given process. In addition, the waste concept changes from its traditional view that waste has no value to one in which waste can be considered as part of an industrial system, and therefore waste has a monetary value that can be defined.

Although considerable progress has been made in incorporating environmental issues into the cost of manufacturing products, there are differences in focus between "end-of-pipe remediation" of the pollution and "design for the environment." The former (remediation) takes the limited viewpoint: "How can I fix the problem?"

"Design for the environment" [21] tries to change the design of the manufacturing process from its inception. It considers that the world has limited resources and puts a social value on air, water, and the Earth's resources. "Design for the environment" assumes that a state must be maintained in which future generations will be able to enjoy the same level of benefits that today's people enjoy. That is, "design for the environment" asks, "How can I make sure from the start that there won't be a problem?"

When thinking in the "forever" time frame, it is obvious that there will be a continuing need for creativity combined with practicality of development of sustainable, driver-friendly, environmentally friendly transportation. No clear future direction to meet this need has yet evolved.

Application of the life-cycle analysis approach to crankcase lubrication issues should help future lubricant developers assess the consequence of various alternative

lubrication options. In addition, it may assist vehicle manufacturers in evaluating long-term tactics for sustainable mobility.

Acknowledgements

The authors thank Robert Stockwell, Jeff Knight, Robert Olree, Coleman Jones, Leonard Sackett, George Ford, and Dennis Meyers of General Motors Powertrain, Steve Cadle and James Spearot of General Motors Research and Development and Planning, and Tom McDonnell of Ethyl Corporation for reviewing and suggesting improvements to this chapter.

REFERENCES

1. Figure derived from information available in PJ Younggren and SE Schwartz. The effects of trip length and service type (synthetic versus mineral oil) on engine damage and engine-oil degradation in a driving test of a vehicle with a 5.7L engine. SAE (Society of Automotive Engineers) Paper no. 932838, 1993.
2. Figure derived from information available in SE Schwartz and CJ Mettrick. Mechanisms of engine wear and engine oil degradation in vehicles using M85 or gasoline. SAE Paper no. 942027, 1994.
3. SE Schwartz. A model for the loss of oxidative stability of engine oil during long-trip service Part I. Theoretical considerations. *STLE Trib Trans* 35(2):235, 1992.
4. SE Schwartz. A model for the loss of oxidative stability of engine oil during long-trip service Part II. Vehicle measurements. *STLE Trib Trans* 35(2):307, 1992.
5. Eur. Patent 57,820. Service interval display for motor vehicle (8/18/92, H Muehlberge, E Starmuehle, W Weishaupt, P Flohr, F Bourauel).
6. RE Kauffman. Development of a remaining useful life of lubricant evaluation technique. III. Cyclic voltammetric methods. *Lubrication Eng* 45:709, 1989.
7. T Kato, M Kawamura. Oil maintenance tester: A new device to detect the degradation level of oils. *Lubr Eng* 42:694, 1986.
8. D Cipris, A Walsh, T Palinasamy. Sensor for motor oil quality. *Proc. Symp. Chemical Sensors* 87(9):401, 1987.
9. U.S. Patent 4,733,556. Method and apparatus for sensing the condition of lubricating oil in an internal combustion engine (1988, AH Meitzler, GS Saloka).
10. U.S. Patent 4,762,476. Development of an automatic engine oil change indicator (5/3/88, SE Schwartz, DJ Smolenski, AJ Wisheart, TN Nguyen).
11. SE Schwartz., DJ Smolenski. Development of an automatic oil-change indicator system. SAE Paper no. 870403, 1987.
12. DJ Smolenski, SE Schwartz, Engine oil condition monitoring. Chapter 80 in ER Booser, ed. *Tribology Data Handbook*. Boca Raton, FL: CRC Press, 1997, pp 927–934.
13. SA Culley, TF McDonnell. The impact of passenger car motor oil phosphorus on engine durability, oil degradation, and exhaust emissions in a field trial. SAE Paper no. 952344, 1995.
14. DJ Ball et al. The impact of passenger motor oil phosphorus levels on automotive emissions control systems. SAE Paper no. 961898, 1996.
15. Guidelines for life-cycle assessment: A code of practice. From the SETAC (Society of Environmental Toxicology and Chemistry) Workshop, Sesimbra, Portugal, March 31–April 3, 1993.
16. S Papasavva et al. Life cycle analysis of automotive powder primers. *Proc 27th Intl Waterborne, High-Solids & Powder Coatings Symp®*, New Orleans, March 1–3, 2000.

17. S Papasavva, W Moomaw. Life cycle global warming impact of CFCs and CFC-substitutes for refrigeration. *Industrial Ecol* 4:71, 1998.
18. I Boustead, BR Yaros, S Papasavva. Eco-labels and eco-indices. Do they make sense? SAE Paper no. 2000-01-1473, 2000.
19. TE Graedel, BR Allenby. *Industrial Ecology and the Automobile*. Englewood Cliffs, NJ: Prentice Hall, 1998.
20. R Socolow, C Andrews, F Berkhout, V Thomas, eds. *Industrial Ecology and Global Change*. Cambridge, UK: Cambridge University Press, 1995.
21. GA Keioleian et al. Application of life cycle inventory analysis to fuel tank system design. *Intl J LCA* 3(1):18, 1998.

Long-Term Trends in Industrial Lubricant Additives

FAY LINN LEE and JOHN J. W. HARRIS

Shell Global Solutions US, Houston, Texas, U.S.A.

1 INTRODUCTION

The formulation of the various types of lubricating oils used in industry vary significantly depending on their application. The types of industrial oil lubricants considered in this chapter, in decreasing order of volumes consumed by industry, are

1. Circulating oils, including turbine oils
2. Hydraulic oils
3. Gear oils
4. Compressor oils

Trends in lubricating grease formulations are also considered.

Performance requirements relevant to each type of lubricant are listed in [Table 1](#). As may be expected, the greater the number of performance properties required of a lubricant, the more complex the formulation.

2 ADDITIVES FOR CIRCULATING OILS AND TURBINE OILS

2.1 Performance Requirements for Circulating Oils and Turbine Oils

The following performance requirements are typically required for circulating oils and, in particular, steam and gas turbine oils:

1. Provide bearing lubrication.
2. Remove heat through circulation.
3. Serve as hydraulic fluid for governor and other control equipment.

Table 1 Performance Requirements for Industrial Oils

Type of oil	Performance property*				
	Rust and oxidation inhibition	Ability to resist foaming	Ability to separate water	Antiwear properties	Extreme-pressure performance
Circulating and turbine oils	X	X	X	—	—
Hydraulic oils	X	X	X	X	—
Compressor oils	X	X	X	X	—
Gear oils	X	X	X	X	X
Lubricating grease	X	—	—	X	X

*"X" indicates performance properties that are commonly required.

4. Lubricate reducing gears.
5. Protect against corrosion.
6. Allow rapid separation of water.
7. Resist foaming.
8. Resist oxidation and sludge formation.

Since gas turbine oils typically operate at higher temperatures than steam turbine oils, requirement 8 is even more critical for gas turbine oils.

Various military and civilian agencies and turbine builders issue specifications for turbine oils [1,2]. Performance tests that usually appear in these specifications are listed in [Table 2](#).

2.2 Additives

The types of additives commonly used in turbine oils are listed in [Table 2](#) with the performance properties they impart and related test methods.

2.2.1 Antioxidants

Antioxidants are used to inhibit the attack of turbine oil by oxygen and to reduce the formation of adverse oxidation products such as corrosive organic acids and insoluble sludge. In turbine oils this is often accomplished with synergistic blends of hindered phenols and diaryl amines, which inhibit oxidation by donating a hydrogen atom to reactive peroxy radical intermediates formed during the oxidation process, thus terminating a chain reaction that would otherwise propagate the degradation of more oil molecules [3–7]. Antioxidants that deactivate peroxy radicals are termed *primary antioxidants*. Volatile antioxidants are generally avoided because they can be depleted by evaporation during use.

Another type of antioxidant inhibits oil oxidation by decomposing reactive hydroperoxide intermediates to less reactive chemical species. Otherwise, these hydroperoxides would decompose to reactive radicals, resulting in the propagation of the oxidation process. Antioxidants that act as peroxide decomposers are termed *secondary antioxidants* [5]. Types of additives that fall into this class include thioethers, zinc dialkyldithiophosphates, zinc dialkyldithiocarmates, and organic phosphites.

Table 2 Additives Used in Turbine Oils

Additive function	Types of additives	Related performance tests
Antioxidant	Diaryl amines Hindered phenols Organic sulfides	ASTM ^a D 1743, Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils ASTM D 2272, Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Bomb ASTM D 4310, Standard Test Method for the Determination of the Sludging and Corrosion Tendencies of Inhibited Mineral Oils ASTM D 6186, Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry, (PDSC)
Rust inhibitor	Alkylsuccinic acid derivatives Ethoxylated phenols Imidazoline derivatives	ASTM D 665, Standard Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water
Foam inhibitor	Polydimethylsiloxanes Polyacrylates	ASTM D 892, Standard Test Method for Foaming Characteristics of Lubricating Oils
Metal deactivator	Triazoles Benzotriazoles 2-Mercaptobenzothiazoles Tolutriazole derivatives	ASTM D 130, Standard Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test
Mild antiwear/ EP additive	Alkylphosphoric acid esters and salts	ASTM D 4172, Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four Ball Method) ASTM D 5182, Standard Test Method for Evaluating the Scuffing Load Capacity of Oils (FZG Visual Method)
Demulsifier	Polyalkoxylated phenols Polyalkoxylated polyols Polyalkoxylated polyamines	ASTM D 1401, Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids

^aAmerican Society for Testing and Materials, Annual Book of ASTM Standards: Petroleum Products, Lubricants and Fossil Fuels, Volumes 5.01–5.04, issued annually.

Industrial oil formulators exploit synergistic relationships between hindered phenols and diaryl amines, and between primary antioxidants and secondary antioxidants [8]. Manufacturers of antioxidants have also developed additives that contain both the phenol moiety and the thioether moiety in the same molecule so that one additive can potentially act both as primary and secondary antioxidant [5].

2.2.2 Rust Inhibitors

Turbine oils are formulated to prevent rust on areas in contact with the oil. Typical turbine oil specifications require that the oil pass corrosion tests using both demineralized and salt water, ASTM D 665, procedures A and B, respectively. Anticorrosion additives are generally polar in nature and preferentially form water-resistant films on iron or steel surfaces [5]. Such additives should not be readily leached from the turbine oil by water entrained in the circulating oil and should not adversely affect other desirable performance properties such as fast water separation and low-foaming tendencies. Types of rust inhibitors that may be used in turbine oils are listed in Table 2.

Rust inhibitor-related compatibility problems can occur if certain turbine oils are contaminated with industrial oils that contain organometallic performance additives. For example, antiwear hydraulic oils may contain zinc-based antiwear additives and metal sulfonate rust inhibitors, and interactions between acidic rust inhibitors in the turbine oil and metal-containing additives in the antiwear hydraulic oil can result in the formation of insoluble salts, which can plug filters. Similarly, if a new turbine component is installed in a unit and metal sulfonate rust preservatives on the part have not been completely washed off, a similar filter-plugging situation can occur.

2.2.3 Metal Deactivators

Metal deactivators prevent corrosion of copper and copper alloys such as bronze and brass. They function by preferentially adsorbing onto the surface of copper alloys, forming a protective layer that inhibits attack by acids formed during oxidation of the bulk lubricant [5,9]. Conversely, the metal deactivator can protect the oil from the catalytic effects of the copper alloy, which could accelerate bulk oil oxidation. Table 2 lists types of copper passivators that may be used in turbine oils.

2.2.4 Foam Inhibitor

Antifoam additives of the type listed in Table 2 are added to turbine oils in order to control foaming tendencies. One method for measuring foaming tendencies is ASTM D 892. Antifoam additives are not completely soluble in oil and form dispersions of tiny droplets of low surface tension that accelerate the coalescence of air bubbles in oil. Typical dose rates for silicone antifoam additives are in the 10- to 20-ppm range while typical dose rates for polyacrylates are in the 50- to 200-ppm range. Because antifoam additives are only partially soluble in oil, they can eventually separate from the oil, resulting in decreased foam control.

It is important that the antifoam additives not adversely affect the air release properties of the turbine oil; otherwise, air entrainment in the oil can result in sluggish operation of hydraulic systems and other problems. Air release is measured by method ASTM D 3427. Typically values of less than 5 to 10 min are desirable. Overdosing with antifoam additive can adversely affect air release properties.

2.2.5 Demulsifiers

Demulsifiers facilitate water separation from oil. They concentrate at the water-oil interface and promote coalescence of water droplets, resulting in faster separation

of water so that it can settle to the bottom of the oil reservoir and be drained off. Types of demulsifiers are listed in [Table 2](#).

2.3 Turbine Oil Monitoring

Despite the use of performance additives, turbine oil properties may deteriorate in use, and guidelines for condemnation values for various physical properties of turbine oils have been developed. Such guidelines are described in ASTM D 4378. Turbine manufacturers may also have their own set of monitoring guidelines for turbine oils.

2.4 Base Oil Effects on Additives

Modern engine oil requirements have driven changes in the mineral oil base stocks available for formulating lubricants, including industrial lubricants. Three of the types of base oils defined by the American Petroleum Institute (API) are described as follows [10]:

1. **Group I** base stocks contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120.
2. **Group II** base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120.
3. **Group III** base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120.

A step-change improvement in the oxidation performance of mineral oil-based turbine oils has been achieved by using Group II base oils in place of Group I base oils. Group II base oils contain significantly lower levels of aromatic compounds, which are susceptible to oxidation, than Group I base oils. However, Group II base oils also contain lower levels of sulfur components, some of which can act as secondary oxidation inhibitors. It has been reported that the oxidation resistance of Group II base oil blends can be further enhanced by adding sulfur-containing secondary oxidation inhibitors along with optimized combinations of hindered phenols and diaryl amine primary antioxidants [8]. Due to the lower solvency of Group II base oils, resulting from the lower levels of aromatic compounds, not all of the additive formulations that performed satisfactorily in Group I base stocks display adequate solubility in Group II base stocks [11].

2.5 Environmental Effects of Turbine Oils

Since turbine oil additives are metal-free and are used at low rates, typically less than 1%, the environmental impact of turbine oil additives is generally fairly minimal. In some cases local wastewater treatment requirements may be such that turbine oil users prefer turbine oils free of detectable phenolic antioxidants.

2.6 Turbine Oils Trends

As the oxidation life of turbine oils is extended, new test methods will be needed to evaluate field performance. New turbine oils formulated with Group II base

oils typically have ASTM D 943 lives between 10,000 and 30,000 hours, making them impractical to characterize by this method. The ASTM D 943 method primarily monitors acid formation as the result of oxidation. Since sludge formation can affect the operation of critical equipment, such as servo-valves, perhaps more emphasis will be placed on measuring the tendency of turbine oils to form sludge and varnish and choosing additives that minimize the formation of insoluble oxidation products. Wider availability of Group III base oils in the future may lead to the development of turbine oil formulations with even longer performance lives.

3 ADDITIVES FOR HYDRAULIC OILS

3.1 Performance Requirements

There are three basic types of hydraulic pumps: gear pumps, vane pumps, and piston pumps. Each is designed to perform specific tasks. Generally, vane pumps operating under high pressure have the greatest requirements for wear protection by hydraulic fluids [12].

The main functions of hydraulic oils are as follows:

1. Transmit power.
2. Protect and lubricate system components.
3. Remove heat through circulation.
4. Protect the components parts from oxidation and corrosion.
5. Provide wear protection.
6. Provide mild EP (extreme-pressure) performance.

Hydraulic oils are expected to meet the following performance requirements:

1. Consistent performance and appropriate viscosity and compressibility
2. Corrosion protection
3. Wear protection and oxidation and thermal stability
4. Hydrolytic stability
5. Long life
6. Filterability
7. Compatibility with system components
8. Good demulsibility or emulsibility, depending on application

The American Society for Testing and Materials has issued a standard specification for mineral oil hydraulic oil, ASTM D 6158. Many pump manufacturers have issued hydraulic oil specifications, which include satisfactory performance under severe conditions in one of the manufacturer's pumps under severe conditions. A number of these specifications have been summarized in the literature [13], as have military specifications for hydraulic oils [2]. Performance tests that often appear in hydraulic oil specifications are listed in [Table 3](#).

3.2 Additives

The types of additives commonly used in hydraulic oils are listed in [Table 3](#).

Table 3 Additives Used in Industrial Hydraulic Oils

Additive function	Types of additives	Related performance tests
Antioxidant	Hindered phenols	ASTM D 1743, Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils ASTM D 2272, Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Bomb ASTM D 4310, Standard Test Method for the Determination of the Sludging and Corrosion Tendencies of Inhibited Mineral Oils ASTM D 6186, Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)
	Diarylamines	
	Phenothiazine	
	Metal dialkyldithiocarbamates	
	Ashless dialkyldithiocarbamates	
	Metal dialkyldithiophosphates	
Rust Inhibitor	Alkylsuccinic acid derivatives	ASTM D 665, Standard Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in Presence of Water
	Ethoxylated phenols	
	Fatty amines	
	Salts of fatty acids and amines	
	Salts of phosphate esters and amines	
	Metal sulfonates	
	Ammonium sulfonates	
Metal deactivator	Imidazoline derivatives	ASTM D 130, Standard Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test
	Benzotriazoles	
	Mercaptobenzimidazoles	
	2-Mercaptobenzothiazoles	
	Thiadiazoles	
Antiwear additive	Tolutriazole derivatives	ASTM D 4172, Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four Ball Method) ASTM D 2882, Standard Test Method for Indicating the Wear Characteristics of Petroleum and Non-Petroleum Hydraulic Fluids in a Constant Volume Vane Pump Various pump tests as specified by pump manufacturers ASTM D 5182, Standard Test Method for Evaluating the Scuffing Load Capacity of Oils (FZG Visual Method)
	Alkylphosphoric acid esters and salts	
	Dialkyldithiophosphates	
	Metal dialkyldithiocarbamates [14]	
	Phosphate esters	
	Dithiophosphate esters	
	Derivatives of 2,5-dimercapto-,3,4-thiadiazoles	
	Molybdenum carboxylates	

Table 3 Continued

Additive function	Types of additives	Related performance tests
Demulsifiers	Polyalkoxylated phenols Polyalkoxylated polyols Polyalkoxylated polyamines	ASTM D 1401, Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids ASTM D 2711, Standard Test Method for Demulsibility Characteristics of Lubricating Oils
Pour point depressants	Poly(alkylmethacrylates)	ASTM D 97, Standard Test Method for Pour Point of Petroleum Products ASTM D 5949, Standard Test Method for Pour Point of Petroleum Products
Foam inhibitors	Polydimethylsiloxanes Polyacrylates	ASTM D 892, Standard Test Method for Foaming Characteristics of Lubricating Oils
Shear stable viscosity index improvers	Poly(alkyl methacrylates) Olefin copolymers Styrene diene copolymers	ASTM D 5621, Standard Test Method for Sonic Shear Stability of Hydraulic Fluids

3.2.1 Antioxidants

In addition to the types of antioxidants described previously for turbine oils, hydraulic oils may use organometallic antioxidants, such as zinc dialkyldithiophosphate (ZDDP) [15,16] additives. The ZDDP additives are multifunctional, acting as secondary antioxidants and as antiwear additives. The types of antioxidants that can be used in hydraulic oils are listed in Table 3.

3.2.2 Rust Inhibitors

Rust inhibitors used in hydraulic oils may contain metals, such as metal sulfonates, and may be overbased in order to provide the capability to neutralize acidic oxidation products. Various rust inhibitors that may be used in hydraulic oils are listed in Table 3.

3.2.3 Antiwear Additives

Antiwear additives are needed to inhibit frictional wear of moving parts, such as the sliding vanes of vane pumps. These additives react with metal surfaces, forming sacrificial films with lower shear strength than the metal itself. The sacrificial films help to reduce friction and, although a small amount of metal is removed with the sacrificial film as it is rubbed off by the moving parts, the rate of metal removal is much lower than if the sacrificial film was not present.

The types of antiwear additives used in hydraulic oils are listed in Table 3. Most hydraulic oil formulations contain ZDDP antiwear additives. The composition of the films that ZDDP additives deposit on metal surfaces has been studied and

determined to be complex [17]. The popularity of these antiwear additives is due to their cost-effectiveness since they are multifunctional, acting both as antiwear additives and as antioxidants. Although ZDDP additives provide excellent antiwear properties, they can also cause corrosion and deposit formation under conditions that promote their hydrolysis or thermal decomposition. By judicious selection of the types of alcohols used to form the phosphate ester portion of the ZDDP molecule, additive developers can maximize hydrolytic and thermal stability while maintaining good antiwear properties. For example, ZDDP antiwear additives derived from primary alcohols have better thermal stability than the corresponding ZDDP antiwear additives derived from secondary alcohols.

Environmentally aware hydraulic oils are formulated with zinc-free, ashless antiwear additives [12,18]. These additives are generally organic compounds containing sulfur and phosphorous. As with the ZDDP antiwear additives, the ashless antiwear additives must be designed in such a way as to maximize hydrolytic and thermal stability as well as antiwear performance. It has been claimed that ashless antiwear oils can exhibit better filterability properties than antiwear oils containing ZDDP [12,19]. Because the possibility exists that ashless and zinc-containing antiwear oils may be inadvertently mixed in commercial applications, it is best to formulate ashless antiwear oils in such a way that they will be compatible with antiwear additives containing ZDDP so that no precipitates are formed that could plug filters [12].

Test methods have been developed to evaluate the thermal and hydrolytic stability of antiwear hydraulic oils. Test method ASTM D 2070 evaluates the thermal stability of an oil by heating the test oil in the presence of copper and iron rods for 168 hr at 135°C. At the end of the test, the metal rods are rated by visual examination and the sludge is isolated by filtration and weighed. Test method ASTM D 2619 evaluates hydrolytic stability by heating and agitating the test oil with water and a copper strip in a sealed glass bottle for 48 hr at 93°C. At the end of the test, the viscosity change of the oil and the acidity changes of the oil and of the water phases are measured, the weight loss of the copper strip is determined, and any resulting insoluble material is isolated and weighed.

3.2.4 Metal Deactivators

Due to the potential corrosiveness of the decomposition products of the antiwear additives, the presence of an effective metal deactivator is even more important in antiwear hydraulic oils than in turbine oils. [Table 3](#) lists types of metal deactivators that can be used in hydraulic oils.

3.2.5 Foam Inhibitor

Because air is compressible, foam or entrained air interferes with the primary function of a hydraulic oil, which is to transfer power. Therefore, the type and amount of silicone or polyacrylate antifoam additive must be carefully chosen to maximize foam inhibition while maintaining good air release properties. Some original equipment manufacturers are extremely concerned about the presence of silicone materials in their plants since it is believed that even a trace of silicone on a metal surface can affect paint coating properties. Therefore, these manufacturers require that only nonsilicone antifoam additives be used in lubricating oils employed in their plants.

The choice of antifoam additive may also be affected by the practice of hydraulic oil condition monitoring. Often optical particle counters based on light scattering techniques are used to monitor oil cleanliness. Since antifoam additives are finely dispersed, partially insoluble fluids in oil, they can falsely be registered as particles by some optical particle counters. In the future, one criterion for choosing antifoam additives may be their ability to disperse sufficiently so as not to interfere with the function of optical particle counters.

3.2.6 Viscosity Index Improver

Viscosity index (VI) improvers are used to widen the useful operating temperature range of hydraulic oils. They are long-chain polymers that function by uncoiling or dissociating at elevated temperatures, resulting in thickening of the oil. Due to this property, oils containing VI improvers will display higher measured kinetic viscosities at elevated temperatures than comparable oils that have the same 40°C oil viscosity but do not contain VI improver. The types of polymers used as VI improvers are listed in [Table 3](#).

An important property of VI improvers for hydraulic oils is shear stability. If a VI improver lacks shear stability, it will quickly be degraded by the hydraulic pump and lose its ability to increase the viscosity of the base oil at elevated temperatures. This will result in less-than-optimum lubricant film thickness and accelerated pump wear. Generally, the shear stability of VI improvers increases as molecular weight decreases. However, the thickening capability of the VI improver also decreases as molecular weight decreases. A trend in the industry is to use VI improvers with better shear stability for better pump protection. Therefore, lower-molecular-weight VI improvers are used even though they must be used at higher percentages by weight.

One method for determining the shear stability of hydraulic oil containing a VI improver, ASTM D 5621, is based on sonic irradiation. In this method a sample of test oil is irradiated in a sonic oscillator for a specified time interval and the change in viscosity after shear is determined. It is claimed that the amount of shear measured by this method is similar to the amount of shear imparted to a hydraulic oil in a hydraulic vane pump test [20].

3.2.7 Pour Point Depressants

Pour point depressant (PPD) additives are chemicals that help mineral oil-based hydraulic oils remain pumpable at low temperatures by lowering the pour point of the oil. The PPD additives are polymers that interfere with the crystallization of wax from mineral oil at low temperatures. By retarding the formation of a wax crystal network in oil at low temperatures, PPDs can reduce the pour points of some paraffinic oils by as much as 30 to 40°C. The effect is less marked in nonparaffinic oils, which have lower wax contents.

3.3 Environmental Concerns

Hydraulic oils have received considerable attention regarding their impact on the environment. Hydraulic oil lines carry oil under moderate to high pressure; therefore, rupture of a line in a forest or near a waterway can result in the release of a significant amount of hydraulic fluid into an environmentally sensitive area. Many agencies have drafted methods for evaluating the environmental impact of

hydraulic oils and for defining what can be classified as a rapidly biodegradable hydraulic oil. For example, the ASTM has issued the following standards and methods related to the evaluation of the impact of hydraulic oils on the environment:

- D 5864, Standard Test Method for Determining the Aerobic Aquatic Biodegradation of Lubricants or Their Components
- D 6006, Standard Guide for Assessing Biodegradability of Hydraulic Fluids
- D 6046, Standard Classification of Hydraulic Fluids for Environmental Impact
- D 6081, Standard Practice for Aquatic Toxicity Testing of Lubricants: Sample Preparation and Results Interpretation.

Generally, biodegradable hydraulic oils are based on natural or synthetic esters. Additives must be chosen that are effective with these types of oils [21] and that are environmentally aware. Regulations governing environmentally aware hydraulic oils generally require that they be metal-free, be readily biodegradable, display low ecotoxicity in water and in soil, and exhibit a low tendency for bioaccumulation [22,23]. This necessitates that the additives used to formulate such hydraulic oils meet most of the same requirements.

3.4 Future Trends

An ongoing trend toward reducing the cost of hydraulic equipment by making it smaller obviates the need for oils that function at higher temperatures and with shorter oil sump residence times. Also, an environmentally driven trend to minimize waste oil disposal will require lubricating oils with longer functional lives. These trends will require oils with improved oxidation resistance, water separation, and air release properties. Some of these improvements will be accomplished by upgrading base oil quality, first from Group I to Group II base oils, and then to Group III base oils. The remainder of the improved performance will be accomplished with improved additives that are also environmentally aware. As base oils are upgraded, changes in additives may also be required to ensure additive–base oil compatibility.

4 ADDITIVES FOR GEAR OILS

4.1 Performance Requirements for Gear Oils

Most industrial operations use equipment driven by one type of gear or other; for example:

- Rock drills
- Crushers
- Hoists
- Mobile equipment
- Grinders
- Mixers
- Speed increases/reducers

There are many combinations of gear types and materials; therefore, the requirements for gear oils are varied [24,25]. Some of the common types of gears are listed in [Table 4](#) and illustrated in [Figures 1 to 7](#). The relative amount of sliding and rolling motion between interacting gears can be quite different between gear types. For example, worm gears interact by a predominantly sliding motion whereas spur gears

Table 4 Common Gear Types

Gear type	Configuration of gear set	Comments
Spur gear (Figure 1)	Straight teeth cut parallel to the axis of the gear	For moderate loads and moderate speeds
Helical gear (Figure 2)	Teeth cut at an angle to the axis of the gear	For higher speeds and higher loads than spur gears Produce axial thrust
Herringbone gear (Figure 3)	Teeth cut in a "V" shape	Similar to helical gear, but the "V" shape of the gears eliminates the axial load
Bevel gear (Figure 4)	Straight teeth cut on an angular surface of a truncated cone	For transfer of motion of shafts where shaft centerlines intersect and shafts are at right angles to each other For moderate loads and moderate speeds
Spiral bevel gear (Figure 5)	Similar to bevel gear except the teeth are cut at an angle on a radial line	For higher speeds and higher loads than bevel gear Quieter operation than bevel gear
Hypoid gear (Figure 6)	Similar to spiral bevel gear, but teeth cut to accommodate shaft centerlines on different planes	For high loads and quiet running Interaction of meshing gear teeth is strictly sliding Tooth loads can be high, requiring gear oil with good extreme-pressure performance
Worm gear (Figure 7)	Gear wheel turning at right angles to an offset worm (screw) gear	Interaction of meshing gear teeth is strictly sliding Tooth loads can be kept low with proper gear tooth design

operate by a combination of rolling and sliding interactions. For straight gears, such as spur gears, only one tooth from each gear supports load at one time. Angled and curved gears are designed to allow more than one gear tooth on each gear to simultaneously support load, resulting in greater load-carrying capacity.

Because the amount of sliding and rolling action and the load-carrying capacity of the various gear types can vary significantly, their gear oil performance requirements can vary substantially. For example, lightly loaded spur gears require an oil with only rust and oxidation inhibitors while heavily loaded hypoid gears require oils with high levels of extreme-pressure additives. In the case of worm gears, their action is almost all sliding, the teeth are generally not heavily loaded, and the smaller worm gears may be made of bronze for better sliding wear resistance. For these types of gears an oil compounded with a friction modifier, such as acidless tallow, may be sufficient.

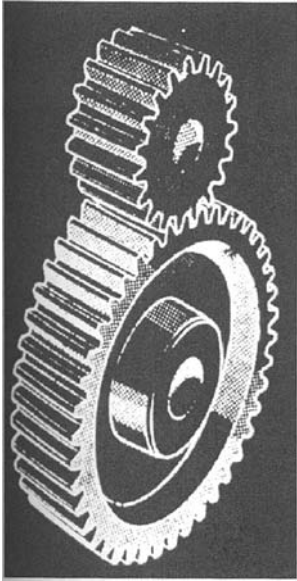


Figure 1 Spur gears. (Courtesy of Lubrizol Corp.)

The American Gear Manufacturers Association (AGMA) provides a series of gear oil specifications for industrial enclosed gear drives and industrial open gearing. The AGMA classifications provide for three types of oil in various viscosity grades. Oils are classified as those containing rust and oxidation inhibitors only, those that

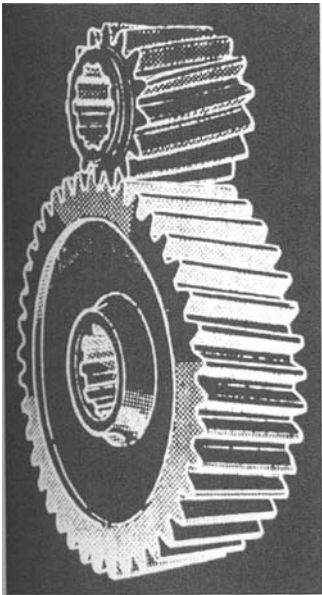


Figure 2 Helical gear. (Courtesy of Lubrizol Corp.)

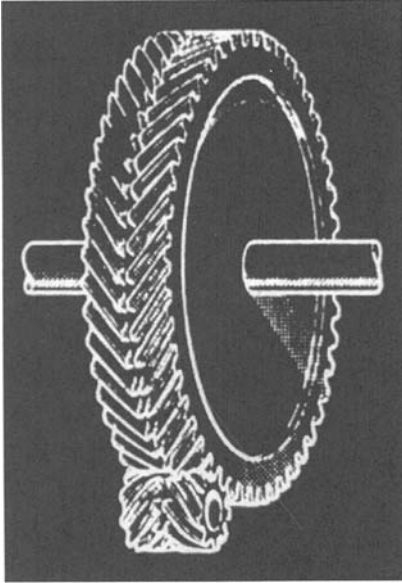


Figure 3 Herringbone gears (double helical). (Courtesy of Lubrizol Corp.)

also contain extreme-pressure additives, and those containing fatty material along with rust and oxidation inhibitors. The fatty material, such as acidless tallow, provides mild extreme pressure and friction reduction for predominantly sliding applications such as worm gears. The types of performance tests that appear in gear oil specifications are listed in [Table 5](#).

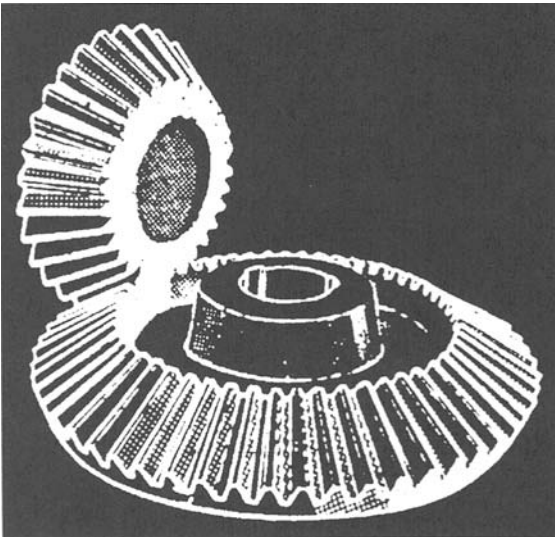


Figure 4 Straight bevel gears. (Courtesy of Lubrizol Corp.)

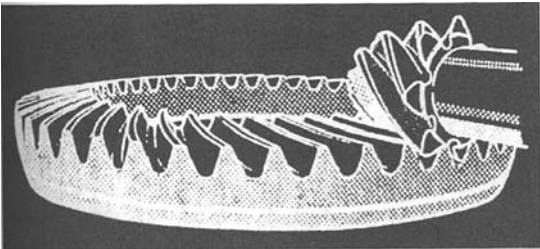


Figure 5 Spiral bevel gears. (Courtesy of Lubrizol Corp.)

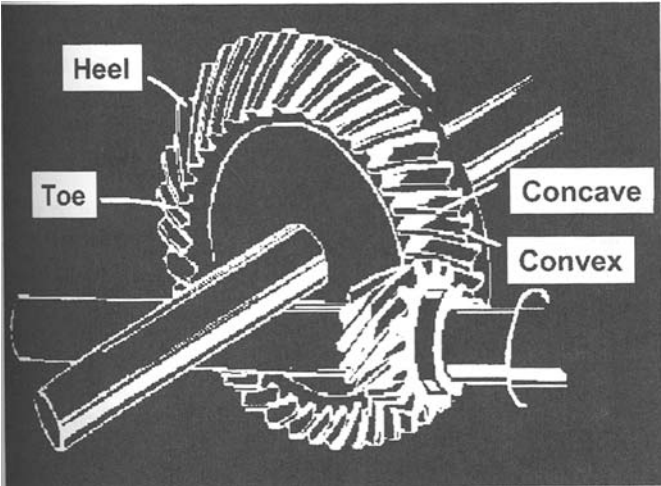


Figure 6 Hypoid gears. (Courtesy of Lubrizol Corp.)

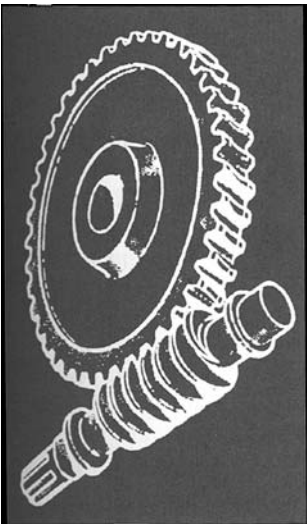


Figure 7 Worm gears. (Courtesy of Lubrizol Corp.)

Table 5 Additives Used in Industrial Gear Oils

Additive function	Types of additives	Related performance tests
Antioxidant	Hindered phenols Diarylamines Phenothiazine Metal dialkyldithiocarbamates Ashless dialkyldithiocarbamates Metal dialkyldithiophosphates	ASTM D 6186, Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC) ASTM D 2893, Standard Test Method for Oxidation Characteristics of Extreme Pressure Lubricating Oils
Rust inhibitor	Alkylsuccinic acid derivatives Ethoxylated phenols Fatty amines Salts of fatty acids and amines Salts of phosphate esters and amines Metal sulfonates Ammonium sulfonates Substituted imidazolines	ASTM D 665, Standard Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in Presence of Water
Metal deactivator	Benzotriazoles Mercaptobenzimidiazoles 2-Mercaptobenzothiazoles Thiadiazoles Tolutriazole derivatives	ASTM D 130, Standard Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test
Antiwear additive	Alkylphosphoric acid esters and salts Dialkyldithiophosphates Metal dialkyldithiocarbamates Phosphate esters Dithiophosphate esters Derivatives of 2,5-dimercapto-1,3,4-thiadiazoles Molybdenum carboxylates	ASTM D 4172, Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four Ball Method)
Soluble extreme-pressure additive	Sulfurized esters [26] Sulfurized olefins [26] Diaryl disulfides [26] Dialkyldithiophosphate esters Lead naphthenate Bismuth naphthenate [27] Antimony dialkyldithiocarbamate Antimony dialkyldithiophosphate Ammonium salts of phosphate esters Chlorinated waxes High-molecular-weight complex esters [28] Borate esters [29]	ASTM D 5182, Standard Test Method for Evaluating the Scuffing Load Capacity of Oils (FZG Visual Method) ASTM D 2782, Standard Test Method for Measurement of Extreme-Pressure Properties of Lubricating Fluids (Timken Method) ASTM D 2783, Standard Test Method for Measurement of Extreme-Pressure Properties of Lubricating Fluids (Four Ball Method)

Table 5 Continued

Additive function	Types of additives	Related performance tests
Solid extreme-pressure additive	Molybdenum disulfide Graphite	See above test methods for extreme-pressure properties, wear preventive properties
Tackifier	Polyisobutylenes	No ASTM standard test method
Demulsifiers	Polyalkoxylated phenols Polyalkoxylated polyols Polyalkoxylated polyamines	ASTM D 1401, Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids ASTM D 2711, Standard Test Method for Demulsibility Characteristics of Lubricating Oils
Friction modifiers	Acidless tallow Long-chain esters Long-chain amides	ASTM D 4857, Standard Test Method for Determination of Coefficient of Friction of Lubricants Using the Four-Ball Wear Test Machine
Pour point depressants	Poly(alkylmethacrylates)	ASTM D 97, Standard Test Method for Pour Point of Petroleum Products ASTM D 5949, Standard Test Method for Pour Point of Petroleum Products
Foam inhibitors	Polydimethylsiloxanes Polyacrylates	ASTM D 892, Standard Test Method for Foaming Characteristics of Lubricating Oils
Shear stable viscosity index improvers	Poly(alkylmethacrylates) Olefin copolymers Styrene diene copolymers	Severe shear tests are under development
Antimisting additives	Polyisobutylenes [30–32]	ASTM D 3705, Standard Test Method for Misting Properties of Lubricating Fluids

4.2 Additives for Gear Oils

The types of additives used in industrial gear oils are listed in Table 5.

Many of the types of additives used in hydraulic oils are also used in gear oils. Additives that differ from those used in hydraulic oils are discussed next.

4.2.1 Extreme-Pressure Additives

Organic sulfur and phosphorous compounds and inorganic borates are primary components in gear oil extreme-pressure additives [33]. The roles of these various elements in gear oil packages have been studied and reviewed [34]. The phosphorus in sulfur/phosphorous extreme-pressure additives yields low wear rates under normal operating conditions while the sulfur prevents seizure under high loads. Modern gear oils often contain borates as well. Finely divided inorganic borates dispersed in gear oil can further enhance load-carrying capacities at high and

low speeds, possibly by forming a chemically bound borate film on the iron surfaces [34].

Combinations of organic phosphorous-and chlorine-containing compounds have also been used as extreme-pressure additives for gear oils. However, it is believed that the low melt temperatures of iron chlorides is a limiting factor as well as the potential for organic chlorides to decompose in the presence of water and yield hydrochloric acid [34].

4.2.2 Friction Modifiers

For applications involving primarily sliding contact, such as worm gears, friction modifiers like acidless tallow may be used. In these applications friction modifiers can be more effective than sulfur-containing extreme-pressure additives, which might promote corrosion of bronze worm gears.

4.2.3 Viscosity Index (VI) Improvers

Because gear oils can be subjected to even greater mechanical shear than hydraulic oils, the polymers used in VI improved gear oils must possess exceptional shear stability. It is preferable to use low-molecular-weight VI improvers in gear oils since low-molecular-weight polymers display greater shear stability than high-molecular-weight polymers. The use of lower-molecular-weight VI improvers increases formulation costs since they must be used at higher percentages than high-molecular-weight VI improvers in order to achieve the same VI increase. Despite the higher costs associated with the use of lower-molecular-weight VI improvers, this approach is necessary in order to maintain gear oil viscosity grade and lubricating film thickness during operation.

4.2.4 Antimisting Additives

Mist lubrication is an effective means of lubricating gears and other elements; however, care must be taken to minimize stray mist, which could cause health problems for those working in the vicinity. Polymeric additives such as polyisobutenes can be used to promote coalescence of oil drops and reduce the formation of stray mist [30–32].

4.3 Additives for Open Gear Lubricants

For large, slow-moving gears that cannot practically be enclosed in oil-tight casings, an adhesive, high-viscosity material is required to stick to the gears. Such open gear lubricants are generally applied by spraying or brushing. In cold climates a synthetic base oil may be required to provide a high-viscosity base fluid that can be sprayed at low temperatures [35,36]. Such lubricants generally contain the following core components:

1. High-viscosity base oil
2. Oil-soluble EP additives
3. Solid EP additives
4. Tackifier
5. Anticorrosion additive.

4.4 Environmental Concerns

In the past, gear oils have contained organic derivatives of lead for extreme-pressure performance, and open gear lubricants have contained chlorinated solvents to improve pumpability. Over the last decade, environmental considerations have essentially resulted in the elimination of these components. Newer open gear lubricant formulations also tend to avoid the use of asphalt on the basis of environmental and performance considerations [35,36].

For applications where industrial gear oils are used in environmentally sensitive areas such as forests and near waterways, biodegradable gear oils based on natural and synthetic esters have been developed [37].

4.5 Future Trends

A failure phenomenon known as *micropitting* has surfaced as a problem in certain applications such as wind turbine gearboxes [38]. Although the failure mode is not completely understood, it is believed to be related to the surface finish of the gears. Test methods have been developed to measure the ability of gear oils to protect against micropitting [39]. There is more to learn in terms of understanding micropitting and minimizing its occurrence.

As in the case of hydraulic pumps, gearbox efficiencies are being improved in order to provide lower operating costs for the end users. This will result in higher gear speeds and loads and higher oil operating temperatures. The challenge for gear oil formulators will be to use base oils and additives that provide

1. Improved thermal stability and cleanliness
2. Improved high-temperature EP performance
3. Improved oxidation resistance
4. Extended demulsibility life
5. Lower friction
6. Improved foam resistance
7. Improved surface fatigue protection

5 ADDITIVES FOR COMPRESSOR OILS

5.1 Performance Requirements for Compressor Oils

It is difficult to generalize the lubrication requirements of compressors since requirements depend on a number of parameters such as the type of compressor, the properties of the gas being compressed, and designed discharge temperatures and pressures [40,41].

Compressors can be classified into two types, positive displacement and dynamic, depending on the process by which they compress gas. Compressors based on positive displacement trap the gas, reduce its volume, then discharge the compressed gas. Dynamic compressors accelerate the gas and convert velocity to increased pressure. Positive-displacement compressors are useful for high-pressure applications with one limiting factor being the discharge gas temperature. Dynamic compressors are useful for high-volume, low-pressure applications.

Positive-displacement compressors can be further classified into reciprocating and rotary compressors. Reciprocating compressors utilize single-acting or double-acting pistons. Rotary types include rotary vane and rotary screw compressors.

Principal sites for lubrication in reciprocating compressors include the crankshaft and associated bearings, connecting rods, wrist pins, pistons, cylinders, piston rings, and valves. Rotary screw compressor lubrication sites include the rotors, bearings, and shaft seals. Rotary vane compressors require lubrication of bearings and shafts [41].

Dynamic centrifugal compressors require lubrication of bearings, gear reducers, and seals [41].

Critical lubrication requirements of the various types of compressors include the following:

1. Oxidation resistance
2. Thermal stability
3. Low carbon deposits at high temperatures (high-pressure reciprocating compressor)
4. Compatibility with gas being compressed
5. Viscosity retention (resistance to dilution by gas being compressed)
6. Antiwear properties (rotary vane)
7. Gas seal provided
8. General lubrication
9. Heat removal
10. Corrosion prevention
11. Compatibility with compressor components
12. Good demulsibility
13. General cleanliness
14. Low-foaming tendencies
15. Low flammability

5.2 Compressor Oil Formulation

High-pressure reciprocating compressors require lubricants stable at high temperatures because discharge temperatures can range from 350 to 500°F. Lubricants for such reciprocating compressors must not generate heavy carbon deposits at hot valve areas since this increases the risk for fires and explosions. Consequently, lubricants for these applications are usually based on synthetic base oils with low carbon-forming tendencies, such as diesters and polyol esters.

Although the requirements for compressor oils vary significantly depending on a number of parameters and a substantial portion of compressors oils are based on synthetic fluids, many formulations still rely on the types of additives listed in [Tables 2](#) and [3](#) for turbine oils and hydraulic oils. Rotary vane compressors require lubricants that minimize vane wear and vane-sticking problems. In addition to the types of additives already mentioned for turbine and hydraulic oils, detergent additives may be used in some rotary vane compressor oils to help prevent deposit formation and vane sticking.

The formulations of compressor oils can vary significantly depending on the type of compressor and the type of gas being compressed. For example, mineral oils

are generally not used for compressing natural gas, because natural gas is soluble in mineral oil. Dilution of mineral oil-based compressor oil with natural gas would decrease the viscosity of the oil below an effective lubricating level. In this case, a polyglycol-based oil with limited solubility for natural gas is more suitable.

5.3 Compressor Oil Trends

Although mineral oil-based lubricants may be suitable for normal duty with non-reactive gases, a variety of synthetic-based lubricants are used for severe-duty, high-temperature, and high-pressure applications and for gases that are reactive with mineral oils. As a general trend, ester-based compressor lubricants are often used for reciprocating compressors in severe service duty due to their lower tendency to form carbon deposits that can lead to fires in reciprocating compressors. For rotary screw and rotary vane compressors, synthetic polyalphaolefins are growing in popularity due to their good thermal stability and lower cost relative to ester-based fluids. The formulation of compressors oils for severe service is so dependent on equipment design and the chemical nature of the gas being compressed that the compressor manufacturers generally designate the compressor oil formulations that are suitable for their equipment.

6 ADDITIVES FOR LUBRICATING GREASES

6.1 Performance Requirements for Lubricating Greases

A lubricating grease consists of a lubricating oil, performance additives, and a thickener, which is a fine dispersion of an insoluble solid that is capable of forming a matrix that retains the oil in a semisolid state. Due to their semisolid consistency, lubricating greases hold some advantages over lubricating oils. A grease is more easily sealed into a bearing than an oil; a grease does not require a circulating system; and in wet or dusty environments, a grease can act as a seal against contaminants. For these reasons, greases are often the preferred lubricant for ball and roller bearings in electric motors, household appliances, mobile equipment wheel and chassis lubrication, and some industrial plain and roller bearings.

Due to the wide variety of applications in which a lubricating grease may be used, there are many different specifications for lubricating greases. Many multipurpose greases meet the LB-GC requirements of ASTM D 4950, Standard Classification and Specification for Automotive Service Greases, which is a classification system that was developed by a cooperative effort of the ASTM, the National Lubricating Grease Institute (NLGI), and the Society of Automotive Engineers (SAE). The ASTM D 4950 specification covers lubricating greases suitable for the periodic relubrication of chassis systems and wheel bearings of passenger cars, trucks, and other vehicles. In the ASTM D 4950 classification system, the letters "LB" signify service typical of lubrication of chassis components and universal joints in passenger cars, trucks, and other vehicles under mild to severe duty. The letters "GC" signify service typical of lubrication of wheel bearings operating in passenger cars, trucks, and other vehicles under mild to severe duty. It is possible to formulate lubricating greases that meet both the LB and GC specifications, and such greases may display the NLGI GC-LB certification mark [42].

Many military grease specifications have been written [2], and greases meeting particular military specifications have been designated for critical applications, such as aviation applications. Additionally, many original equipment manufacturers, such as automobile manufacturers, issue specifications for greases that are specifically for the equipment that they build.

The main ingredient that differentiates a grease from an oil is the grease thickener. Most grease thickeners are soaps comprised of the reaction product of a fatty acid derivative and a metallic hydroxide. Other salts may be combined with the soap thickeners to impart higher grease dropping points (temperature at which the grease liquefies). Such greases are called *complex greases*. A smaller proportion of lubricating greases are manufactured with nonsoap thickeners such as organoclays or polyurea compounds. Some of the more common thickeners are listed below:

1. Lithium salt of hydrogenated castor oil fatty acid
2. Calcium stearate (hydrous)
3. Calcium stearate anhydrous
4. Lithium complex
5. Aluminium complex
6. Calcium complex
7. Organoclay
8. Polyurea
9. Silica

6.2 Additives

Performance additives for greases are similar to those used in lubricating oils; however, it is important that the grease additives also be compatible with the grease thickener. Lack of compatibility between an additive and a grease thickener could lead to a disruption of the thickener matrix that holds the oil in a semisolid state. This would result in an uncontrolled softening or hardening of the grease or a decrease in the grease dropping point.

The various grease thickeners behave differently with respect to their compatibility with performance additives. Generally, lithium soap thickener is compatible with a much wider variety of grease additives than organoclay thickener. Consequently, an anticorrosion additive like a calcium sulfonate may perform quite well in a lithium soap-thickened grease, whereas it could cause significant softening of an organoclay-thickened grease. Therefore, performance additives must be carefully matched with the type of grease thickener.

The levels at which additives are used in lubricating greases are generally higher than in lubricating oils. Several factors can contribute to the need for higher additive addition rates in lubricating greases as compared to lubricating oils:

1. The grease thickener may compete with the performance additive for adsorption sites on the metal surfaces.
2. The grease thickener may adsorb additive so that less is available for performing the desired additive function.
3. Compared to lubrication by circulating oil, grease lubrication does not provide a mechanism for heat removal and the reserve of lubricant is much less.

Another difference between lubricating oils and greases, in terms of additive use, is that lubricating greases can more readily utilize solid additives. Although attempts have been made to suspend various dispersions of solid additives in lubricating oils, such lubricants generally suffer from a tendency to separate or plug filters. However, the semi solid consistency of greases is such that they can easily keep fine solid lubricants, like graphite and molybdenum disulfide, suspended indefinitely.

The types of additives used in greases are listed in [Table 6](#) along with corresponding test methods used to evaluate the performance properties these additives impart to the grease.

6.2.1 Rust and Oxidation Inhibitors

Greases for lightly loaded and high-speed applications rely on elasto-hydrodynamic lubrication and generally require only rust and oxidation inhibitors and antiwear additives. The types of additives used to achieve these performance properties are similar to those used in lubricating oils ([Table 6](#)). As previously mentioned, the additives may be used at higher percentages in lubricating grease than are typically used in lubricating oils.

Unlike oil formulators, grease formulators are not restricted to performance additives that give clear and bright solutions in oil. Even insoluble additives, such as sodium nitrite and sodium sebacate, have been used as rust inhibitors in greases. A drawback of solid additives is that they can contribute to higher noise levels in grease-lubricated bearings [51].

6.2.2 Antiwear and Extreme-Pressure Additives

For mobile equipment and industrial bearings where heavier loads are involved and where the oil film may not be sufficient to prevent metal-to-metal contact, extreme-pressure and antiwear additives, such as those listed in [Table 6](#), are used. These additives include most of the types used in EP gear oil formulations.

As indicated by the extreme-pressure test methods listed in [Table 6](#), there are several methods for measuring the extreme-pressure properties of greases. These test methods differ in the way that they evaluate antiwear and extreme-pressure performance and, therefore, it is desirable to develop grease formulations that perform well in all these test methods when designing multipurpose industrial greases. This is usually accomplished by using more than one additive and taking advantage of synergistic effects between the additives [52]. It has been reported that the performance of some extreme-pressure additives may be affected by the temperature at which they are added to the grease. For example, the Timken OK load (ASTM D 2509) of a lithium base grease appeared to increase from 35 lb to 55 lb when the temperature of addition of the sulfurized olefin extreme-pressure additive was raised from 90°C to 120°C [53].

In applications where shock loading may occur, such as the bearings of large shovels and certain conveyor bearings, the rapid application of load could cause scoring of metal surfaces before soluble extreme-pressure additives could react to form a sacrificial layer. Solid lubricants are used in such applications to provide a physical separation of metal surfaces during shock loading. Such lubricants are usually finely dispersed solid that have the ability to form films on metal surfaces that decrease sliding friction. Various solid lubricants that have been used in

Table 6 Additives Used in Lubricating Greases

Additive function	Types of additives	Related performance tests
Antioxidant	Hindered phenols	ASTM D 5483, Standard Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry
	Diarylaminines	
	Phenothiazine	
	Oligomers of trimethyldihydroquinoline	ASTM D 942, Standard Test Method for Oxidation Stability of Lubricating Grease by the Oxygen Bomb Method
	Metal dialkyldithiocarbamates	
	Ashless dialkyldithiocarbamates	
Rust inhibitor	Metal dialkyldithiophosphates	ASTM D 1743, Standard Test Method for Corrosion Preventive Properties of Lubricating Greases
	Alkylsuccinic acid derivatives	
	Ethoxylated phenols	
	Nitrogen-containing heterocyclic compounds	ASTM D 5969, Standard Test Method for Corrosion preventive Properties of Lubricating Greases in the Presence of Dilute Synthetic Sea Water Environments
	Fatty amines	
	Salts of fatty acids and amines	
	Salts of phosphate esters and amines	ASTM D 6138, Standard Test Method for Determination of Corrosion Preventive Properties of Lubricating Grease Under Dynamic Wet Conditions (Emcor Test)
	Metal sulfonates [43,44]	
	Ammonium sulfonates	
	Substituted imidazolines	
	Lead naphthenate	
	Bismuth naphthenate	
Metal deactivator	Sodium nitrite	ASTM D 4048, Standard Test Method for Detection of Copper Corrosion from Lubricating Greases
	Sodium sebacate	
Antiwear additive	Disalicylidene-propanediamine	ASTM D 5707, Standard Test Method For Measuring Friction and Wear Properties of Lubricating Grease Using a High-Frequency, Linear-Oscillating (SRV) Test Machine
	Derivatives of 2,5-dimercapto-1,3,4-thiadiazole	
	Alkylphosphoric acid esters and salts	ASTM D 2266, Standard Test Method for Wear Preventive Characteristics of Lubricating Grease (Four Ball Method)
	Dialkyldithiophosphates	
	Metal dialkyldithiocarbamates	
	Phosphate esters	
	Dithiophosphate esters	
Soluble extreme-pressure additive	Derivatives of 2,5-dimercapto-1,3,4-thiadiazoles	ASTM D 5706, Standard Test Method for Determining Extreme Pressure Properties of Lubricating Greases Using a High-Frequency, Linear-Oscillation (SRV) Test Machine
	Molybdenum carboxylates	
	Sulfurized esters [26]	
	Sulfurized olefins [26]	
	Diall disulfides [26]	
	Organic sulfur/phosphorous compounds	
	Lead naphthenate	
	Bismuth naphthenate [27,45]	

Table 6 Continued

Additive function	Types of additives	Related performance tests
	Antimony dialkyldithiocarbamate	ASTM D 2596, Standard Test
	Antimony dialkyldithiophosphate	Method for Measurement of
	Ammonium salts of phosphate esters	Extreme Pressure Properties of Lubricating Grease (Four Ball Method)
	Chlorinated waxes	
	High-molecular-weight complex esters	ASTM D 2509, Standard Test
	Borate esters [46]	Method for Measurement of Load Carrying Capacity of Lubricating Grease (Timken Method)
Solid extreme-pressure additive	Metal borates	See above test methods for extreme-pressure properties and friction and wear properties
	Molybdenum disulfide [47]	
	Perfluorinated polyolefins	
	Graphite [48]	
	Calcium carbonate	
	Calcium phosphate	
	Calcium acetate	
	Boron nitride	
	Boric acid	
	Metal powders	
	Phosphate glasses [49]	
Tackifier	Polyisobutylenes	No standard test method
Polymers for water resistance	Atactic polypropylene	ASTM D 4049, Standard Test
	Polyethylene	Method for Determining the Resistance of Lubricating Grease to Water Spray
	Functionalized polyolefins [50]	
	Alkylsuccinimides	ASTM D 1264, Standard Test
	Polyisobutenes	Method for Determining the Water Washout Characteristics of Lubricating Greases
	Styrene butadiene block copolymers	

lubricating greases are listed in Table 6. Perhaps the two most commonly used solid lubricants in greases are graphite and molybdenum disulfide. Synergistic extreme-pressure effects between these two solid lubricants have been exploited in greases and open gear lubricants for a number of years [54]. It has also been claimed that the extreme-pressure/antiwear performance of graphite can be enhanced by treatment of graphite with polar agents, such as alkali molybdates and tungstennates and alkali earth sulfates and phosphates. Treatment of graphite with these polar inorganic materials helps the graphite to adhere to metal surfaces more strongly, even in the absence of trace water, which is normally necessary for untreated graphite to adhere to metal, and act as a friction-reducing lubricant [55].

Specialized semifluid grease containing solid lubricants have been developed for the lubrication of open gears that cannot be lubricated by means of an oil reservoir [56]. These greases are required to produce a sturdy protective film on

heavily loaded gears that may also be subjected to shock loading. The grease is usually applied at intervals through a spray nozzle and therefore must be readily pumpable and sprayable. In the past, pumpability has been achieved by the addition of solvent such as 1,1,1-trichloroethane or a hydrocarbon solvent. More recently solvent-free open gear greases have been developed using synthetic base oils to achieve low-temperature performance and pumpability [56]. Open gear greases generally contain combinations of soluble extreme-pressure additives and solid lubricants in order to achieve high extreme-pressure performance. These lubricants may also contain high levels of polymers to promote adhesion and water resistance. Open gear greases are usually gray to black in color due to the presence of graphite and molybdenum disulfide; however, light-colored open gear greases have been developed through the use of colorless solid lubricants such as phosphate glass [49].

Thread compounds are another example of specialty greases that contain high levels of solid lubricants. These compounds are generally composed of grease combined with a very high level of metal powder and other solid lubricants. For example, API Bulletin 5A2 [57] describes a thread compound composed of 36% w grease, 47.5% w lead powder, 19.3% w zinc powder, 5.2% w copper powder, and 28% w natural graphite. Thread compounds may also be formulated with anticorrosion additive in order to protect pipe threads during storage.

6.2.3 Polymers for Water Resistance

Mobile equipment is often used in applications where grease lubricated bearings may be subjected to water, as are bearings in certain industrial applications such as in steel and paper mills. It has been found that the addition of various polymers to lubricating greases improves their water resistance. Some of the types of polymers that have been used to impart water resistance to lubricating greases are listed in Table 6. While most of these polymers improve water resistance by raising the grease base fluid viscosity, at least one functionalized polymer actually reacts with alkali during the formation of the soap thickener and becomes a part of the grease thickener matrix [58].

6.2.4 Grease Thickeners as Performance Additives

A recent development in the evolution of lubricating grease technology has been the use of solids that act both as grease thickeners and as performance additives. For example, a number of patents have been written concerning the preparation and use of calcium sulfonate complex greases where calcium carbonate dispersed by calcium sulfonate acts as thickener, anticorrosion additive, and extreme-pressure additive [59,60]. Similar multifunctional claims have been made for greases thickened with specially designed titanium complex thickeners [61,62].

6.3 Environmental Concerns

Environmental concerns and regulations have influenced modern grease formulations, and this trend will likely accelerate in the future. The disposal of lubricants that contain restricted substances is onerous and expensive. Therefore, there has been a shift away from additives that appear on restricted substance lists or that

may appear on future restricted substances lists. Examples of formulation changes instigated primarily by environmental concerns include the following:

1. Substitution of alternative extreme-pressure and anticorrosion additives to replace lead naphthenates and lead dialkyldithiocarbamates
2. Removal of heavy-metal powders from thread compounds [63–65]
3. Removal of chlorinated solvents from open gear lubricants and greases [56]
4. Substitution of alternative extreme-pressure and antiwear additives to replace chlorinated paraffins [28,66]
5. Substitution of alternative anticorrosion additives to replace sodium nitrite

Concern was raised in California over the possible toxicity of the solid lubricant molybdenum disulfide. This could have been a problem for the disposal of used grease containing molybdenum disulfide. However, after toxicological review, the California Department of Toxic Substances Control ruled that wastes containing molybdenum in the form of molybdenum disulfide are excluded from identification as hazardous waste [67].

Various original equipment manufacturers, such as automobile manufacturers, provide long lists of restricted substances that are not allowed in materials, such as lubricants, which they purchase. There is not much doubt that the list of restricted substances will grow in the future.

Concerns about environmental persistence will likely increase the demand for biodegradable greases. Although the market for this type of grease is currently quite modest, the U.S. Army has written a specification for biodegradable multipurpose grease that should help to advance the technology [68]. Such greases usually contain natural or synthetic ester base oils that are biodegradable and additives of low toxicity that, if not readily biodegradable themselves, at least do not impede the ability of microorganisms to ultimately biodegrade organic portions of the grease to carbon dioxide, water, and biomass. Studies have been performed to determine the effectiveness of various grease additives in these types of base greases [69,70].

6.4 Lubricating Grease Trends

As in the case of other industrial lubricants, the trend for lubricating greases is to develop products with improved high-temperature performance leading to longer bearing lives. Grease formulators are also searching for anticorrosion additives that provide better protection against salt-water corrosion and that do not significantly affect the performance of the grease thickener [44].

Because interaction of grease additives and grease thickener must be considered for the development of optimum grease formulations, it follows that the importance of various grease additives may change as the popularity of the various grease thickeners changes. While the versatility of lithium soap and lithium complex greases causes them to be the most widely used grease types, polyurea greases are growing in popularity since they tend to give significantly longer bearing lives in certain sealed bearing applications. It is expected that the popularity of polyurea- and diurea-thickened greases will continue to grow, and, as they do, more emphasis will be placed on developing additives that perform optimally with these types of thickeners.

REFERENCES

1. I Macpherson, DD McCoy. Hydraulic and turbine oil specifications. In ER Booser, ed. *Tribology Data Handbook*. 1997, Boca Raton, FL; CRC press, pp 279–281.
2. BD McConnell. Military specifications. In ER Booser, ed. *Tribology Data Handbook*. Boca Raton, FL; CRC press, 1997, pp 182–241.
3. ET Denisov, IV Kyudyakor. *Chem Rev* 1313–1357, 1987.
4. M Rasberger. Oxidative degradation and stabilization of mineral oil based lubricants. *Chemistry and Technology of Lubricants*. London: Blackie Academic & Professional, 1992.
5. PC Hamblin, U Kristen, D Chasan Ardsley. Ashless antioxidants, copper deactivators and corrosion inhibitors: Their use in lubricating oils. *J Lubr Sci* 2(4):287–318, 1989.
6. JR Thomas, CA Tolman. Oxidation inhibition by diphenylamine. *J Amer Chem Soc* 84:2930–2935, 1962.
7. JR Thomas. The identification of radical products from the oxidation of diphenylamine. *Amer Chem Soc* 82:5955–5956, 1960.
8. VJ Gatto, MA Grina. Effects of base oil type, oxidation test conditions and phenolic antioxidant structure on the detection and magnitude of hindered phenol/diphenylamine synergism. *Lubrication Eng* 55(1):11–20, 1999.
9. Y Luo, B Zhong, J Zhang. The mechanism of copper-corrosion inhibition by thiadiazole derivatives. *Lubr Eng* 51(4):293–296, 1995.
10. American Petroleum Institute, Appendix E—API (base oil interchangeability guidelines for passenger car motor oils and diesel engine oils. API) 1509, 14th ed., Addendum 1, 1998, p E-1.
11. AS Galliano-Roth, NM Page. Effect of hydroprocessing on lubricant base stock composition and product performance. *Lubrication Eng* 50(8):659–664, 1994.
12. D Clark et al. New generation of ashless top tier hydraulic fluids. *Lubrication Eng* 56(4):22–31, 2000.
13. I Macpherson, DD McCoy. Hydraulic and turbine oil specifications. *Tribology Data Handbook*. Boca Raton, FL: CRC Press, 1997, pp 274–278.
14. DK Tuli et al. Synthetic metallic dialkyldithiocarbamates as antiwear and extreme-pressure additives for lubricating oils: Role of metal on their effectiveness. *Lubr Eng* 51(4):298–302, 1995.
15. MD Sexton. Mechanisms of antioxidant action. Part 3. The decomposition of 1-methyl-1-phenylethyl hydroperoxide by OO'-dialkyl(aryl)phosphorodithioate complexes of cobalt, nickel, and copper. *J Chem Soc: Perkin Trans II* 1771–1776, 1984.
16. AJ Bridgewater, JR Dever, MD Sexton. Mechanisms of antioxidant action. Part 2. Reactions of zinc bis-[OO'-dialkyl(aryl)phosphorodithioates] and related compounds with hydroperoxides. *Chem Soc: Perkin Trans II* 1006–1086, 1980.
17. JM Georges et al. Mechanism of boundary lubrication with zinc dithiophosphate, *wear* 53:9–34, 1979.
18. WB Bowden, JY Chien, KA Colapret. Scrapping downtime in a scrapyards—a field test of ashless hydraulic oils in a high pressure application. *Lubrication Eng* 54(11):7–11, 1998.
19. LR Kray, JH Chan, KM Morimoto. New direction for paper machine lubricants, ashless vs. ash type additive formulations. *Lubr Eng* 51(10):834–838, 1995.
20. RL Stambaugh, RJ Kopko, TF Roland. Hydraulic pump performance—a basis for fluid viscosity classification, SAE Paper no. 901633.
21. S Asadauskas, JM Perez, JL Duda. Oxidative stability and antiwear properties of high oleic vegetable oils. *Lubr Eng* 52(12):877–892, 1996.
22. RL Goyan, RE Melley, WC Ong. Biodegradable lubricants. *Lubr Eng* 54(7):10–17, 1998.

23. DE Tharp, KD Erdman, GH Kling. Development of the BF-1 biodegradable hydraulic fluid requirements. *Lubr Eng* 54(7):21–23, 1998.
24. VW Castleton. Development and use of multipurpose gear lubricants in industry. *Lubr Eng* 51(7):593–598, 1995.
25. RW Cain, PS Greenfield, GF Hermann. Industrial gear oil: Past, present and future. *NLGI Spokesman* J 64(8):22–29, 2000.
26. O Rohr. Sulfur: The ashless additive, sulfur as a key element in EP greases and in general lubricants. *NLGI Spokesman* 58(5):20–27, 1994.
27. RW Hein. Evaluation of bismuth naphthenate as an EP additive. *Lubr Eng* 56(11):45–51, 2000.
28. PR Miller, H Patel. Using complex polymeric esters as multifunctional replacements for chlorine and othe additives. *Lubr Eng* 53(2):31–33, 1997.
29. J Yao, J Dong. Improvement of hydrolytic stability of borate esters used as lubricant additives. *Lubr Eng* 51(6):475–478, 1995.
30. JP Maxwell. Practical application of oil mist lubrication for gear driven machine tool heads. *Lubr Eng* 49(6):435–437, 1993.
31. K Bajaj. Oil-mist lubrication of high-temperature paper machine bearings. *Lubr Eng* 50(7):564–568, 1994.
32. RS Marano et al. Polymeric additives as mist suppressants in metal cutting fluids. *Lubr Eng* 53(10):25–34, 1997.
33. M Masuko, T Hanada, H Okabe. Distinction in antiwear performance between organic sulfide and organic phosphate as EP additives for steel under rolling with sliding partial EHD conditions. *Lubr Eng* 50(12):972–976, 1994.
34. SM Kim et al. Boundary lubrication of steel surfaces with borate, phosphorous, and sulfur containing lubricants at relatively low and elevated temperatures. *Trib Trans* 43(4):569–578, 2000.
35. DB Barret, IR Bjel. High viscosity gels for heavy duty open gear drives ... a break from tradition. *Lubr Eng* 49(11):820–827, 1993.
36. G Daniel et al. Lubricants for open gearing. *NLGI Spokesman* 63(6):20–30, 1999.
37. BR Hohn, K Michaelis, R Dobereiner. Load carrying capacity properties of fast biodegradable gear lubricants. *Lubr Eng* 55(11):15–38, 1999.
38. J Muller. The lubrication of wind turbine gearboxes. *Lubr Eng* 49(11):839–843, 1993.
39. P Oster, H Winter. Influence of the lubricant on pitting and micro pitting resistance of case carburized gears—test procedures. AGMA paper 87-FTM-9, 1987.
40. W Scales. Air compressor lubrication. In ER Booser, ed. *Tribology Data Handbook*. Boca Raton, FL: CRC Press, 1997, pp 242–247.
41. KC Lilje, RE Rajewski, EE Burton. Refrigeration and air conditioning lubricants. In ER Booser, ed. *Tribology Data Handbook*. Boca Raton, FL: CRC Press, 1997, pp 342–354.
42. *Lubricating Grease Guide*, published by the National Lubricating Grease Institute, 4th ed., 1996, pp 3.28–3.36.
43. R Baker. A comparison of rust inhibitors in ASTM D 1743 and IP 220 tests. *NLGI Spokesman* 57(9):20–23, 1993.
44. ME Hunter, F Baker. Corrosion rust and beyond. *NLGI Spokesman* 63(1):14–20, 1999.
45. O Rohr. Bismuth, the new and “green” extreme pressure-element and the best replacement for lead. *NLGI Spokesman* 61(6):10–17, 1997.
46. U.S. Pat. 5, 242, 610, Grease composition (1993, JP Donor).
47. TJ Risdon. EP additive response in greases containing MoS₂. *NLGI Spokesman*, 63(8):10–19, 1999.
48. WM Kenan. Characteristics of graphite lubricants. *NLGI Spokesman* 56(11):14–17, 1993.
49. L Tocci. Transparent grease bears a heavy load. *Lubes-n-Greases* 3(4):52, 1997.

50. U.S. Patent 5,110,490, Water resistant grease composition (1992, HS Pink, T Hutchings, JF Stadler).
51. CE Ward, CE Littlefield. Practical aspects of grease noise testing. *NLGI Spokesman* 58(5):8–12, 1994.
52. S Beret. Assessment of grease EP Performance and EP testing. *NLGI Spokesman* 58(8):7–22, 1994.
53. PR Todd, MR Sivik, GW Wiggins. An investigation into the performance of grease additives as related to the temperature of addition: Part 1. *NLGI Spokesman* 64(3): 14–18, 2000.
54. FG Fischer, AD Cron, RG Huber. Graphite and molybdenum disulphide-synergisms. *NLGI Spokesman* 46(6): 190, 1982.
55. R Holinski, M Jungk. New solid lubricants as additives for greases—“polarized graphite”. *NLGI Spokesman* 64(6):23–27, 2000.
56. N Samman, SN Lau. Grease-based open gear lubricants: Multi-service product development and evaluation. *Lubr Eng* 55(4):40–48, 1999.
57. API Bulletin 5A2 on Thread compounds for casing, tubing, and line pipe, 5th ed. Issued by American Petroleum Institute, 1972.
58. C Scharf, HF George. The enhancement of grease structure through the use of functionalized polymer systems. *NLGI Spokesman* 59(8):8, 1996.
59. U.S. Pat. 5, 308, 514 Sulfonate greases (1994, WD Olsen, RJ Muir, T Eliades, T Steib).
60. W Macwood, R Muir. Calcium sulfonate greases ... one decade later. *NLGI Spokesman* 63(5):24–37, 1999.
61. A Mukar et al. A new generation high performance Ti-complex grease. *NLGI Spokesman* 58(1):25–30, 1994.
62. A Kumar et al. Titanium complex greases for Girth gear application. *NLGI Spokesman* 63(6):15–19, 1999.
63. WD Stringfellow, NL Jacobs, RV Hendricks. Environmentally acceptable specialty lubricants, an interpretation of the environmental regulations of the North Sea. *NLGI Spokesman* 57(9): 14–19, 1993.
64. N Adamson, JM Pinoche, T Noel. A novel tubing/casing thread compound offering both corrosion protection and performance with environmental acceptability. *NLGI Spokesman* 62(7):10–22. 1998.
65. U.S. Patent 5, 180,509, Metal-free lubricant composition containing graphite for use in threaded connections (1993, NL Jacobs).
66. RJ Fensterheim. Where in the world are chlorinated paraffins heading. *Lubes-n-Greases* 4(4):14, 1998.
67. J Dumdum. Government regulations update. *NLGI Spokesman* 58(4):36, 1994.
68. I Rhee. 21st century military biodegradable greases. *NLGI Spokesman*. 64(1):8–17, 2000.
69. A Fessenbecker, I Roehrs, R Pagnoglou. Additives for environmentally acceptable lubricant. *NLGI Spokesman* 60(6):9–25, 1996.
70. N Kato et al. Lubrication life of biodegradable greases with rapeseed oil base. *Lubr eng* 55(8): 19–25, 1999.

Long-Term Additive Trends in Aerospace Applications

**CARL E. SNYDER, JR., LOIS J. GSCHWENDER AND
SHASHI KANT SHARMA**

*United States Air Force Research Laboratory, Materials and Manufacturing
Directorate, Wright–Patterson Air Force Base, Ohio, U.S.A.*

1 UNIQUE REQUIREMENTS FOR AEROSPACE APPLICATIONS

Aerospace, especially military aerospace systems, requires faster, highly maneuverable, and higher-temperature systems. The higher temperatures typically experienced in aerospace applications are common for all lubricants, but we use hydraulic fluids as an example. The high temperatures experienced in aerospace hydraulic systems are the result of three related factors. First, for military aircraft the operational requirements for the aircraft (e.g., high speed, high degree of maneuverability) impose more severe demands on the hydraulic systems. Second, weight is always a critical issue for aircraft that drives hydraulic system components that are small and operate under more strenuous conditions (e.g., higher speed, higher loads) and that imposes more severe operating conditions on the hydraulic fluid (i.e., higher temperatures, higher shear rates). Third, the high emphasis on weight savings for aircraft applications results in smaller fluid volume systems. All these factors result in higher temperatures being imposed on the hydraulic fluids. While the first factor is usually not an issue for commercial aerospace applications, the other two are equally important. In addition to the higher temperatures imposed on aerospace hydraulic fluids, they must also be capable of operating at extremely low temperatures. Aircraft hydraulic and lubrication systems are required to operate at temperatures as low as -54°C . Typical operational temperature ranges for the hydraulic fluids used in aerospace are shown in [Figure 1](#). Similar factors make unique demands on other aerospace lubricants, such as gas turbine engine oil, greases, etc. Aerospace

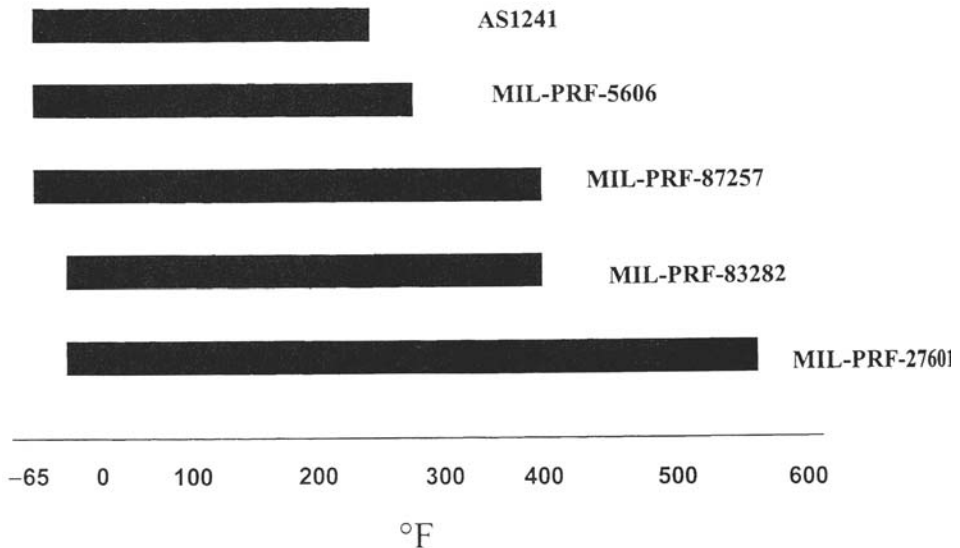


Figure 1 Temperature ranges for aerospace hydraulic fluids.

applications include both spacecraft and aircraft applications. The major emphasis of this chapter is aircraft applications. Hydraulic fluids and gas turbine engine oils are discussed in this chapter because they represent the larger volume usage, but similar factors and issues exist for the other aerospace lubricants and fluids such as greases and coolants. Liquid and grease lubricants for space applications are also discussed because the space environment creates some unique and challenging problems for lubricant additives. Often the customary additives are not adequate for aerospace applications, and more development is needed to make acceptable aerospace lubricants [1–8].

2 WHY ARE ADDITIVES NEEDED?

Additives are required for aerospace fluids and lubricants to enhance or impart a required operational capability to a specific fluid or lubricant not provided by the base fluid alone. When a lubricant (lubricating oil, hydraulic fluid, and grease, etc.) is stressed in its operating environment, it can degrade such that the performance of the system or component in which it is used is adversely affected. In order to enhance the performance of a lubricant, or to mitigate its degradation during use, additives are required. Some of the additive types used in aerospace applications are listed below. Depending on the application, a formulation may contain one or more of these and other additives:

1. Boundary lubrication additives (antiwear, lubricity, extreme-pressure)
2. Antioxidants
3. Anticorrosion additives
4. Metal deactivators

A lubricant has to be effective in both the fluid-film lubrication and the boundary lubrication regimes. In fluid-film lubrication, a fluid film separates the

Table 1 Typical Additives Used in Aerospace Fluids and Lubricants

Fluid additive	Gas turbine engine oil	Hydraulic fluid		Space lubricant	
		Hydrocarbon	Phosphate ester	Hydrocarbon	PFP AE
Antioxidant	Aromatic amines, e.g., PANA	Hindered phenol	*	Hindered phenol	Experimental
Lubricity/antiwear	Aryl phosphate	Aryl phosphate	*	Aryl phosphate	Experimental
Viscosity index	N/A	Polymethyl methacrylate	*	N/A	—
Rust inhibitor	Metal sulfonate or organic acid	Metal sulfonate	*	N/A	NaNO ^{2**}
Antifoam	Silicone	Silicone	*	N/A	N/A
Metal deactivator	Benzotriazole	Benzotriazole	*	N/A	N/A

*Proprietary.

**Greases only.

N/A – Not typically used for this application.

interacting surfaces, while in boundary lubrication, more direct contact occurs between the two surfaces. Fluid-film lubrication can be further divided into two broad categories—hydrodynamic lubrication and elasto-hydrodynamic lubrication. In fluid-film lubrication, the physical properties of the lubricant such as viscosity, pressure viscosity, and traction determine the performance of the lubricated contact. While fluid-film lubrication is the desired mode of operation, the boundary lubrication regime cannot be avoided. Even in fluid-film lubrication, boundary lubrication occurs during the start-up and stopping, and during occasional asperity interaction during operation. Therefore, the material (both the surfaces and the lubricant) properties important for the boundary lubrication regime are equally important for the fluid-film lubrication. Boundary lubrication additives are generally needed for reducing friction and wear of the components [9].

Antioxidants are required to prolong the useful life of fluids and lubricants. Most fluids and lubricants are hydrocarbon-based and are susceptible to oxidative degradation via a free-radical mechanism. Antioxidants react with the initially produced free radicals to prevent the oxidation process from proceeding from the slow initiation phase of the process to the rapid autocatalytic phase.

Corrosion inhibitors are usually synonymous with rust inhibitors for most lubricants. However, as we go to more exotic metals and with the emergence of halogenated lubricants, corrosion can occur with nonferrous metals and by attack of very aggressive fluid degradation products. For example, degradation products from perfluorinated polyalkylethers react with a variety of metals to cause what one could call corrosion. A better definition of corrosion inhibitors would be additives, which inhibit the reaction of moisture or fluid degradation products with metals. They are widely used for that function in many classes of fluids and lubricants.

Metal deactivators are additives, which passivate the surface of metals. The passivation can result in either reducing the metal's catalytic effect on lubricant degradation or reducing the effect of the lubricant on the surface of the metal. They are widely used in hydraulic fluids and lubricants.

3 HOW ADDITIVES WORK

In general, certain performance-improving additives are optimized for specific base oils, but in some instances the same additive can be effective in a variety of classes of base fluids. However, in some cases additives that have been effective at improving a specific property or performance parameter in one or several classes of base fluids are not effective in others. For example, substituted aryl phosphates have been very effective antiwear additives for steel-on-steel rubbing contacts in a large number of chemical base stocks, e.g., mineral oils, synthetic hydrocarbons, esters, and even more exotic base fluids such as the polyphenyl ethers and the silahydrocarbons. They are not effective additives, however, for steel-on-steel contacts in polydimethyl siloxanes or chlorotrifluoroethylene lubricants. The reason for specificity of some additives is beyond the scope of this chapter, but it is important to recognize this phenomenon as we consider future trends for additive applications. As we attempt to develop advanced lubricants using new and novel base oils, we must recognize that new additive technology may be required. How different additives enhance the performance of a lubricant is discussed ahead.

In boundary lubrication the interacting surfaces react with the lubricant components to form protective physisorbed, chemisorbed, or reaction films [10]. When metal-to-metal contact occurs between two surfaces in a lubricated contact, the asperities on the surfaces shear, thereby exposing a fresh metal surface. The appropriate lubricant component reacts with the exposed fresh metal to form protective surface films. The surface films thus formed are generally low-friction and wear-resistant and protect the surfaces from early failure/wear. During operation these surface films can wear and regenerate. Antiwear or lubricity additives are generally added to the base oil to enhance the formation of the protective surface films during boundary lubrication. Thus, in boundary lubrication the chemistry of the lubricant along with the material properties of the interacting surfaces determine the performance of the lubricated contact.

Many researchers have expended significant effort at determining the detailed mechanism by which specific additives work. In some cases, e.g., the free-radical interceptor mechanism of most effective antioxidants, the mechanisms have been intensively studied, worked out, and generally well understood [11]. In other cases, however, although extensive research has been conducted, e.g., the mechanism of action of tricresyl phosphate, there are a number of theories, many of which are supported by chemical data, but no one theory is universally accepted.

When one reviews the published data and, in the case of many researchers, their unpublished data, a few common facts can be found for many types of performance-improving additives. First, most additives appear to be effective through a "competitive reaction" mechanism. In other words, the additive is reacting with some undesirable species that occurs in the lubrication system that, if unchecked, will lead to premature failure of the lubricant or component. In the case of an antioxidant in a hydrocarbon lubricant, the additive is reacting with the initial free radicals formed early in the oxidation process to retard or prevent their attack on the lubricant molecules in an autocatalytic process that results in rapid deterioration of the lubricant. In the case of the antiwear additives in hydrocarbon lubricants, the additive reacts with the newly formed high-energy, fresh metal surfaces formed by metal-to-metal contact, thereby passivating these surfaces by forming, in most cases, lubricious reaction products that prevent the catastrophic wear of the component. The chemistry of that reaction product will vary depending on the chemistry of the additive and the surface. The mechanism of wear protection, however, may vary with lubricants and surfaces of different chemistries, as we discuss later in this chapter.

Another common factor with many is that the additives are generally unreactive and stable during the "normal" functioning of the lubricant and only become effective and reactive on demand. For example, antioxidants in hydrocarbons become effective and reactive only when free radicals are formed in the lubricant due to oxidation of the lubricant molecules. Similarly, effective antiwear additives in hydrocarbon lubricants generally do not react until the fresh metal surfaces are formed. Whether this reaction is induced by the reactivity of the fresh metal surface or the momentary high temperatures that occur during the metal-to-metal contact is an item still under debate, but it is generally accepted that the additive, until this reactivity is triggered by a specific event, is inactive and stable. Something occurs to lower the activation energy and allows the additive to be effective.

Other additives are less affected by “events” that trigger their action. For example, viscosity index improvers [12] and rust inhibitors are generally effective during the entire life of the lubricants and do not require some specific (unusual) event to trigger their actions. But as we consider future additive requirements for future classes of base fluids and surfaces requiring lubrication, new additive technology must be developed.

An additive may work by more than one mechanism. For example, many metal-alkylated sulfonate rust inhibitors form a physical barrier on metal surfaces. The polar portions of the molecules are adsorbed on the metal, effectively blocking water from the corrosion-prone surfaces [8]. The molecules also form micelles or groups of molecules loosely in rings with their polar portions toward the middle. These act as little water traps to surround and tie up water molecules and, again, to prevent them from getting to the metal surfaces.

4 ADDITIVES FOR SPACE APPLICATIONS

Lubricants for outer-space applications are particularly challenging. First of all, the volume of space lubricants used is so small that major oil companies have little interest in investing in research, development, and commercialization, even if the lubricants command a high price. Fortunately, several companies deal with specialty lubricants and are willing to supply to this niche market.

The most important additive for a space lubricant is an antiwear additive [7]. Spacecraft mechanisms generally operate on a very small quantity of lubricant. With lubricant depletion due primarily to evaporation or lubricant creep, the lubricated components experience a higher degree of boundary lubrication. Effective antiwear additives are required for prolonged life of these components. As a general rule, perfluoropolyalkylether (PFPAE) lubricants are not used in applications where the bearing contact stress is over 100,000 psi because they may undergo tribocorrosion-induced failure. An antioxidant is often used to protect a spacecraft hydrocarbon oil and its antiwear additive for the time the formulation is on the Earth, waiting for launch, but is not essential in space, where little oxygen is available.

The major technical challenges for spacecraft lubricant additives are low volatility and good solubility. Spacecraft lubricants were originally mineral oils/greases, but these are gradually being replaced with synthetics including hydrocarbon poly-alphaolefins (PAOs) and multialkylated cyclopentane (MAC) (Pennzane®), and PFPAEs. Even lower volatility and improved low-temperature viscosity silahydrocarbon fluids are in development for spacecraft [13]. Soluble and effective additives are readily available for terrestrial hydrocarbon oils and, with some looking, commercially available low-volatility additives may also be found. In greases, solubility is less important, but it is generally believed that at least partially soluble additives are advantageous in grease performance over nonsoluble additives.

For many years there were no soluble additives for PFPAE lubricants. Conventional additives are not soluble in PFPAE fluids. Solubilizing substituents, similar to the backbone structure of PFPAE fluids, are required in the additive structure to make it soluble in PFPAE fluids. However, PFPAE manufacturers have recently offered soluble additives for their fluids. These additives are made for use in the manufacturers' own product lines and are not available by themselves. The U.S. Air Force has conducted research and development of soluble additives for PFPAE

fluids as part of a High-Performance Turbine Engine Technology program [14]. Additives are needed for PFPAE fluids because of their unique behavior especially in boundary lubrication in low-humidity environments [15]. A phenomenon called *tribocorrosion* can occur that is a combination of fluid decomposition and wear metal corrosion. This happens at much lower temperatures than are predicted by static, nonwear stability tests. The additives act to interrupt the cycle of fluid decomposition and metal interaction, thereby minimizing the tribocorrosion and improving wear performance [16].

Besides antiwear additives, antirust additives are needed to prevent steel components from rusting when used with PFPAE fluids or greases. Conventional hydrocarbon lubricants tend to leave a protective film on the surface of steels, while PFPAE fluids do not, thus leaving low-chrome steel components prone to rusting after use with a PFPAE fluid. This is due to the high solubility of oxygen into the PFPAE fluids, which allows oxygen to get to the iron surfaces, leading to rust.

Several important new classes of additives were developed in the Air Force program, [14] most notably a perfluoroalkyldiphenylether (DPE), a perfluoroalkyltriphenylether (TPE), and a tri(perfluoropolyalkyletherphenyl)phosphine (PH3) [17]. These provide improved antiwear and high-temperature stability to the PFPAE fluids by interacting with and neutralizing fluid decomposition products that, without the additives, attack metal surfaces and cause an autocatalytic decomposition of the fluid.

As the molecular weight of any lubricant increases, the solubility for polar additives decreases. This is especially true for the very nonpolar PAOs. Long-chain alkyl groups on the additives improve additive solubility but often reduce effectiveness. Additives, in general, are polar compounds, which is what makes them effective. All of this makes for a very short list of effective, soluble, and low-volatility additives for spacecraft.

The spacecraft lubricant additives do not need to be especially thermally stable since the spacecraft mechanisms do not operate at high temperatures. They may, however, operate at extreme cold temperatures, and the additives must stay in solution in oils.

Test method for spacecraft lubricants are not well standardized and often are peculiar to a particular satellite company. Because there are few second chances in spacecraft lubricants once in operation, usually a “life test” is conducted for years on Earth under high vacuum to simulate actual operation.

5 ADDITIVES FOR HYDRAULIC FLUIDS

Hydraulic fluids are operated in closed systems, although the fluid reservoir may be open to air. Hydraulic fluid additives may include antioxidant, antiwear, rubber swell, viscosity index improver, and minor amounts of metal deactivator and dye. (This is a simpler list than that of engine oil, where thermal-oxidative stability is critical.) The application temperature often dictates the additives used. Hydraulic fluids for military applications are defined by the military specifications including MIL-PRF-5606H [18] (mineral oil based fluid), MIL-PRF-83282D [19] and MIL-PRF-87257 [20] (both synthetic hydrogenated polyalphaolefin-based fluids). Hydraulic fluids for commercial aircraft are defined by SAE AS 1241 [21].

Antioxidants are usually ashless (containing no metals) and are believed to serve primarily to protect the fluid in storage rather than in an application. A test such as ASTM D 4636, Corrosiveness and Oxidation Stability of Aircraft Turbine Engine Lubricants, and Other Highly Refined Oils, is often used to evaluate the antioxidant effectiveness.

Arylphosphate antiwear additives in hydraulic fluids are widely used and are very effective for steel-on-steel rubbing surfaces. The ASTM D 4172, Wear Preventive Characteristics of Lubricating Fluids (Four-Ball Wear Method), is widely used to evaluate antiwear additives, but other methods are also used.

Rubber swell additives are used with synthetics such as PAOs that, by themselves, provide little swell or even shrinkage to nitrile seals, the most widely used seal material in military aircraft. Nitrile seals were originally developed to swell an appropriate volume with naphthenic mineral oil. When synthetic PAOs were introduced, they had to be adjusted to be a drain-and-fill replacement for mineral oils, so rubber swell additives were added to the synthetic formulations. Rubber swell additives are usually polar esters actually adsorbed into the elastomeric compounds, creating a positive seal to the hydraulic system. Seal tests may include swell per FED-STD-791 method 3603 and other physical property determinations.

Viscosity index (VI) improvers are used mainly with naphthenic mineral and phosphate ester oils to increase the viscosity index (lower the amount of change in viscosity with temperature). They are long-chain polymers such as polymethylmethacrylates, but other chemical classes are also used. In theory, they are coiled at low temperature and strung out at higher temperature and therefore impede flow less at lower temperatures but more at higher temperatures. The VI improvers do impede flow in bulk, such as past seals, and provide additional fluid-film thickness in low-shear environments, but do little to improve the fluid-film thickness in the elastohydrodynamic regime in bearings. VI improvers are broken into smaller pieces in high-shear and high-stress environments, present in both elasto-hydrodynamic and boundary lubrication regimes, and therefore become less effective. A shear stability test, for example as in the MIL-PRF-5606 hydraulic fluid specification [18] is used to determine a formulation's resistance to shear under a specific set of conditions, but this test does not duplicate the severity of real lubricated contacts.

A minor amount (0.05%) of metal deactivator is needed with PAO based oils for a hydraulic fluid to pass all the metal weight changes in ASTM D 4636. A small amount of dye is used in hydraulic fluids for leak detection. Hydrocarbon hydraulic fluids are usually dyed red, while phosphate ester hydraulic fluids are dyed purple.

6 ADDITIVES FOR GAS TURBINE ENGINE OILS

Aircraft engine oils must have a critical balance of performance-improving additives, especially if used at high temperatures. Engine oils are often sprayed onto hot bearings with considerable airflow present to help cool the bearing. This gives rise to hot spots and thin oil films with lots of contact with oxygen. Coking of the fluid and additives, when they oxidize and turn to carbonaceous deposits, is detrimental to the cooling efficiency of the engine. Also, coke can clog the breathing and oil delivery tubes in an engine.

Engine oils are very oxidatively stable polyol ester-based with one or more antioxidant, and antiwear, antifoam, and metal deactivator additives. All the

additives must have a low propensity to form coke. Often the optimized oil represents a compromise between low cooking and optimum performance as provided by specific additives. For example, different aryl phosphate antiwear additives exhibit various degrees of effectiveness, and it may not be possible to select the best antiwear additive because its presence in the oil causes too much coke formation. As a rule, the coking tendencies of formulations are greater with the more effective aryl phosphates and greater with higher percentages of additive.

An antifoam additive, a specific molecular-weight-range dimethyl silicone, may be used.

The following tests are generally used to evaluate the effectiveness of the additives:

Oxidative Stability: ASTM D 4636

Antiwear Performance: ASTM D 1947, Ryder Gear Test and
Modified ASTM D 5182, FZG Test

Anticoking Performance: Fed-Std 791, Method 3450, Bearing Deposition

Foaming: Fed-Std 791, Method 3213, Foaming Characteristics of Aircraft
Turbine Engine Oils (Static Foam Test)

In addition to these tests, each new engine oil qualified to a military specification must pass an actual engine test as described in the specifications.

7 FUTURE TRENDS

Three major factors will drive the need for new additive research and development for aerospace applications. The first one, which has been discussed in detail in the Introduction, is the need for additives effective over a wide temperature range, going from as low as -54°C to over 300°C . The second has already been discussed to some extent, and that is the new classes of base oils developed to meet new, more demanding requirements. The class discussed earlier, the perfluoropolyalkylethers, sometimes called perfluoroethers or perfluoropolyethers, is only one example. Another class that demonstrated unique requirements is the chlorofluorocarbon oligomers that served as the base fluid for a -54°C to 175°C nonflammable aerospace hydraulic fluid. Although most additives typically used in hydrocarbon-based lubricants are quite soluble in the chlorofluorocarbon base stock, most of them have no beneficial effect. The successful development of an effective formulation using that unique base fluid required years of research. The final formulation that met the Military Specification MIL-H-53119 [22] utilized a carefully balanced additive package composed of a lubricity additive and a rust-inhibiting additive. While these are two new and unique base fluids with which the authors have first-hand experience, other new base stocks could be developed for future applications that also require new additive research and development.

The third factor that will prompt the development of new performance-improving additives for future lubricating systems is the change in the chemistry of the surfaces with which the lubricants will come in contact and be expected to lubricate and provide long life. The main type of additive influenced by this factor is the lubricity additive. Two examples are new metal alloys and surface modifications such as hard coatings. In both cases the atoms, which in the past have been available to interact with the additive, are not available or are not readily available.

The chemical reactions that activate the additive are halted. On the other hand, the surface modifications may provide a barrier for any undesirable interaction between the lubricant and the substrate material. New bearing materials such as Cronidur-30®, Rex20® (CRU20®), CCS42L® [23] have been developed that are corrosion-resistant and/or harder than the traditional tool-steel bearing materials such as M50 and 52100. Higher hardness of these new bearing materials gives them higher load-carrying capability. For high-speed precision bearings, hybrid bearings, utilizing the lower-density silicon nitride rolling elements, are gaining popularity.

The lack of reactivity of these materials with the environment (including the lubricant/additive system), that provides them corrosion resistance, also inhibits the formation of the beneficial surface films for enhanced boundary lubrication performance. The state-of-the-art boundary additives, such as tricresylphosphate, are not optimized for the newer chemical composition bearing steels. In order to fully realize the benefits of the new corrosion-resistant/harder bearing steels, new additives will be required. Similar additive development will be required for optimized performance of bearings utilizing hard coatings on the balls and/or races. These hard, wear-resistant coatings, such as TiCN (titanium carbonitride) [24] and TiC (titanium carbide) coated balls, have been shown to extend the lifetime of bearings in critical applications, but in most cases they have been used either with no liquid/grease lubricant or with lubricants optimized for steel-to-steel contacts. Again, the chemistry of the lubricity additives was optimized to react with fresh steel (iron) asperities caused by contact in boundary lubrication. With the changed chemistry of the surface of the bearing material from iron-based alloys to a hard coating, the typical lubricity additives may not effectively provide the significant increase in lifetime as is typically experienced with the steel bearings. In many cases, improved lifetimes are experienced with hybrid bearings that incorporate a coated or ceramic ball and a standard steel race, but with a fully ceramic bearing or one that uses coated surfaces on both the ball and the race, the maximum enhancement in performance cannot be experienced unless new additives are developed that can beneficially interact with these new bearing surfaces to produce the lubricious coatings that are believed to be the main mechanism resulting in the currently experienced wear improvement in steel bearings with the state-of-the-art lubricity additives.

REFERENCES

1. CE Snyder Jr, LJ Gschwender. Development of a nonflammable hydraulic fluid for aerospace applications over a -54°C to 135°C temperature range. *Lubr Eng* 36:458–465, 1980.
2. CE Snyder Jr et al. Development of high temperature (-40° to 288°C) hydraulic fluids for advanced aerospace applications. *Lubr Eng* 38:173–178, 1982.
3. GA Beane IV et al. Military lubricants for aircraft turbine engines. Proc 60th Meeting of Structures and Materials Panel, AGARD, NATO, 1985.
4. CE Snyder Jr et al. Development of a shear stable viscosity index improver for use in hydrogenated polyalphaolefin-based fluids. *Lubr Eng* 42:547–557, 1986.
5. LJ Gschwender, CE Snyder Jr, GA Beane IV. Military aircraft 4 cst gas turbine engine oil development. *Lubr Eng* 42:654–659, 1987.
6. LJ Gschwender et al. Advanced high-temperature air force turbine engine oil program. In WR Herguth, TM Warne, eds. *Turbine Lubrication in the 21st Century*, ASTM STP 1407. West Conshohocken, PA: American Society for Testing and Materials, 2001.

7. LJ Gschwender et al. Improved additives for multiply alkylated cyclopentane-based lubricants. *Trib Trans*. In press.
8. LJ Gschwender et al. Computational chemistry of soluble additives for perfluoropolyalkylether liquid lubricants. *Trib Trans* 39:368–373, 1996.
9. CE Snyder Jr et al. Liquid lubricants and lubrication. In B Bhushan, ed. *CRC Handbook of Modern Tribology*, Vol. I. Boca Raton, FL: CRC Press, 2000 pp 361–382.
10. J Liang, B Cavdar, SK Sharma. A study of boundary lubrication thin films produced from a perfluoropolyalkylether fluid on M-50 surfaces. I. Film species characterization and mapping studies. *Trib Ltrs* 3:107–112, 1997.
11. RK Jensen et al. *Intl J Chem Kinet* 22:1095–1107, 1990.
12. SK Sharma, N Forster, LJ Gschwender. Effect of viscosity index improvers on the elastohydrodynamic lubrication characteristics of a chlorotrifluoroethylene and a polyalphaolefin fluid. *Trib Trans* 36:555–564, 1993.
13. WR Jones et al. The tribological properties of several silahydrocarbons for use in space mechanisms. NASA/TM-2001-211196, Nov 2001.
14. LJ Gschwender, CE Snyder Jr, GW Fultz. Soluble additives for perfluoropolyalkylethers liquid lubricants. *Lubr Eng* 49:702–708, 1993.
15. LS Helmick et al. The effect of humidity on the wear behavior of bearing steels with $R_fO(n-C_3F_6O)_xR_f$ perfluoropolyalkylether fluids and formulations. *Trib Trans* 40:393–402, 1997.
16. SK Sharma, LJ Gschwender, CE Snyder Jr. Development of a soluble lubricity additive for perfluoropolyalkylether fluids. *J Syn Lub* 7:15–23, 1990.
17. U.S. Patent 4,011,267. Perfluoroalkylether substituted aryl phosphines and their synthesis (Mar 1977, C Tamborski, CE Snyder, Jr).
18. MIL-PRF-5606H Military specification, hydraulic fluid, petroleum base; aircraft, missile and ordnance. June 7, 2002.
19. MIL-PRF-83282D Performance specification, hydraulic fluid, fire resistant, synthetic hydrocarbon base, metric. NATO Code Number 537, Sept 30, 1997.
20. MIL-PRF-87257 Military specification, hydraulic fluid, fire resistant; low temperature synthetic hydrocarbon base, aircraft and missile. Dec 8, 1997.
21. AS1241 Fire resistant phosphate ester hydraulic fluid for aircraft. SAE, 1992.
22. MIL-H-53119 Military specification, hydraulic fluid, nonflammable, chlorotrifluoroethylene base. March 1, 1991.
23. *Bearing Steels: Into the 21st Century*, ASTM STP 1327. JJC Hoo, WB Green, eds. American Society for Testing and Materials, 1998.
24. AK Rai et al. Performance evaluation of some pennzane-based greases for space applications. Published in the 33rd Aerospace Mechanisms Symposium Proc. NASA/CP-1999-209259, 1999, pp 213–220.

PART IV

METHODS AND RESOURCES

Summary of Lubricant Standard Test Methods and Some Product Specifications

LESLIE R. RUDNICK

*The Energy Institute, The Pennsylvania State University, University Park,
Pennsylvania, U.S.A.*

This chapter contains a selection of many of the most commonly used test methods and specifications selected from the United States, Europe, and Japanese Lubricant Testing Methods. These include methods, standards, and specifications from ASTM, FTM, MIL, CEC, DIN, and JPI, and Federal Supply Class 9150 commodities. Some cross references are also given.

The American Society for Testing and Materials publishes an Annual Book of ASTM Standards: Petroleum Products, Lubricants and Fossil Fuels, Volumes 5.01–5.04, where a complete list of ASTM methods pertaining to lubricants may be found.

Summary of Standard Test Methods and Specifications

ASTM

D 86	Standard Test Method for Distillation of Petroleum Products
D 88	Standard Test Method for Viscosity Saybolt Seconds Universal
D 92	Standard Test Method for Flash and Fire Points by Cleveland Open Cup
D 93	Standard Test Method for Flash Point by Pensky-Martens Closed Tester
D 95	Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation
D 97	Standard Test Method for Pour Point of Petroleum Products

ASTM (Continued)

D 130	Standard Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test
D 156	Standard Test Method for Saybolt Color of Petroleum Products (Saybolt Chromometer Method)
D 189	Standard Test Method for Conradson Carbon Residue of Petroleum Products
D 217	Standard Test Method for Cone Penetration of Lubricating Grease
D 287	Standard Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hygrometer Method)
D 445	Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)
D 482	Standard Test Method for Ash from Petroleum Products
D 524	Standard Test Method for Ramsbottom Carbon Residue of Petroleum Products
D 566	Standard Test Method for Dropping Point of Lubricating Grease
D 567	Standard Test Method for Calculating Viscosity Index
D 611	Standard Test Method for (1993)el Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents
D 664	Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration
D 665	Standard Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water
D 874	Standard Test Method for Sulfated Ash from Lubricating Oils and Additives
D 892	Standard Test Method for Foaming Characteristics of Lubricating Oils
D 893	Standard Test Method for Insolubles in Used Lubricating Oils
D 942	Standard Test Method for Oxidation Stability of Lubricating Grease by the Oxygen Bomb Method
D 943	Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils
D 972	Standard Test Method for Evaporation Loss of Lubricating Greases and Oils
D 974	Standard Test Method for Acid and Base Number by Color-Indicator Titration
D 1091	Standard Test Methods for Phosphorus in Lubricating Oils and Additives
D 1092	Standard Test Method for Measuring Apparent Viscosity of Lubricating Greases
D 1093	Standard Test Method for Acidity of Hydrocarbon Liquids and Their Distillation Residues
D 1159	Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration
D 1160	Standard Test Method for Distillation of Petroleum Products at Reduced Pressure
D 1209	Standard Test Method for Color of Clear Liquids (Platinum Cobalt Scale) (APHA Color)
D 1238	Standard Test Method for Flow Rates of Thermoplastics by Extrusion Plastimeter (Melt Index) (or ISO 1133–1991)
D 1264	Standard Test Method for Determining the Water Washout Characteristics of Lubricating Greases
D 1296	Standard Test Method for Odor of Volatile Solvents and Diluents
D 1298	Standard Test Method for (1990)el Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

ASTM (Continued)

D 1331	Standard Test Method for Surface and Interfacial Tension of Solutions of Surface Active Agents
D 1358	Standard Test Method for (1995)el Spectrophotometric Diene Value of Dehydrated Castor Oil and Its Derivatives
D 1401	Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids
D 1403	Standard Test Methods for Cone Penetration of Lubricating Grease Using One-Quarter and One-Half Scale Cone Equipment
D 1478	Standard Test Methods for Low-Temperature Torque of Ball Bearing Grease
D 1500	Standard Test Method for Color of Petroleum Products (ASTM Color Scale)
D 1646	Standard Test Method for Rubber Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)
D 1662	Standard Test Method for Active Sulfur in Cutting Oils
D 1742	Standard Test Method for Oil Separation from Lubricating Grease During Storage
D 1743	Standard Test Method for Corrosion Preventive Properties of Lubricating Greases
D 1744	Standard Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent
D 1748	Standard Test Method for Rust Protection by Metal Preservatives in the Humidity Cabinet
D 1831	Standard Test Method for Roll Stability of Lubricating Grease
D 2007	Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum Derived Oils by the Clay-Gel Absorption Chromatographic Method
D 2070	Standard Test Method for Thermal Stability of Hydraulic Oils
D 2155	(discontinued 1981, replaced by E 659)
D 2161	Standard Practice for Conversion of Kinematic Viscosity to Saybolt Universal Viscosity or to Saybolt Furoil Viscosity
D 2265	Standard Test Method for Dropping Point of Lubricating Grease over Wide Temperature Range
D 2266	Standard Test Method for Wear Preventive Characteristics of Lubricating Grease (Four Ball Method)
D 2270	Standard Test Method for Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 and 100°C
D 2272	Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Bomb
D 2273	Standard Test Method for Trace Sediment in Lubricating Oils
D 2500	Standard Test Method for Cloud Point of Petroleum Oils
D 2509	Standard Test Method for Measurement of Load Carrying Capacity of Lubricating Grease (Timken Method)
D 2595	Standard Test Method for Evaporation Loss of Lubricating Greases over Wide Temperature Range
D 2596	Standard Test Method for Measurement of Extreme-Pressure Properties of Lubricating Grease (Four Ball Method)
D 2602	(replaced by D 5293), Standard Test Method for Apparent Viscosity of Engine Oils at Low Temperature Using the Cold-Cranking Simulator
D 2620	(discontinued 1993, replaced by D 5293)
D 2622	Standard Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry

ASTM (Continued)

D 2625	Standard Test Method for Determining Endurance Life and Load Carrying Capacity of Dry Solid Film Lubricants (Falex Method)
D 2670	Standard Test Method for Measuring Wear Properties of Fluid Lubricants (Falex Method)
D 2710	Standard Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration
D 2711	Standard Test Method for Demulsibility Characteristics of Lubricating Oils
D 2766	Standard Test Method for Specific Heat of Liquids and Solids
D 2782	Standard Test Method for Measurement of Extreme-Pressure Properties of Lubricating Fluids (Timken Method)
D 2783	Standard Test Method for Measurement of Extreme-Pressure Properties of Lubricating Fluids (Four-Ball Method) (Load Wear Index)
D 2879	Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope
D 2882	Standard Test Method for Indicating the Wear Characteristics of Petroleum and Non-Petroleum Hydraulic Fluids in a Constant Volume Vane Pump
D 2887	Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography
D 2893	Standard Test Method for Oxidation Characteristics of Extreme-Pressure Lubricating Oils
D 2896	Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration
D 2982	Standard Test Method for Detecting Glycol-Base Antifreeze in Used Lubricating Oil
D 2983	Standard Test Method for Low-Temperature Viscosity of Automotive Fluid Lubricants Measured by Brookfield Viscometer
D 3120	Standard Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
D 3228	Standard Test Method for Total Nitrogen, in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method
D 3232	Standard Test Method for Measurement of Consistency of Lubricating Greases at High Temperatures
D 3233	Standard Test Method for Measurement of Extreme Pressure of Fluid Lubricants (Falex Method)
D 3238	Standard Test Method for Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method
D 3244	Standard Test Method for Standard Practice for Utilization of Test Data to Determine Conformance with Specifications
D 3336	Standard Test Method for Life of Lubricating Greases in Ball Bearings at Elevated Temperatures
D 3525	Standard Test Method for Gasoline Diluent in Used Gasoline Engine Oils by Gas Chromatography
D 3527	Standard Test Method for Life Performance of Automotive Wheel Bearing Grease
D 3704	Standard Test Method for Wear Preventative Properties of Lubricating Grease Using the (Falex) Block on Ring Test Machine in Oscillating Motion
D 3705	Standard Test Method for Misting Properties of Lubricating Fluids
D 3711	Standard Test Method for Deposition Tendencies of Liquids in Thin Films
D 3829	Standard Test Method for Predicting the Borderline Pumping Temperature of Engine Oil

ASTM (Continued)

D 3945	Standard Test Method for Shear Stability of Polymer-Containing Fluids Using Diesel Injector Nozzle (Deactivated 1998, replaced by D6278)
D 4047	Standard Test Method for Phosphorus in Lubricating Oils and Additives by Quinoline Phosphomolybdate Method
D 4048	Standard Test Method for Detection of Copper Corrosion from Lubricating Greases
D 4049	Standard Test Method for Determining the Resistance of Lubricating Grease of Water Spray
D 4057	Standard Test Method for Standard Practice for Manual Sampling of Petroleum and Petroleum Products
D 4172	Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method)
D 4294	Standard Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy
D 4310	Standard Test Method for to Determination of the Sludging and Corrosion Tendencies of the Inhibited Mineral Oils
D 4485	Standard Test Method for Standard Specification Performance of Automotive Engine Oils
D 4624	Standard Test Method for Measuring Apparent Viscosity by Capillary Viscometer at High-Temperature and High Shear Rates
D 4628	Standard Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry
D 4629	Standard Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection
D 4636	Standard Test Method for Corrosion and Oxidative Stability of Hydraulic Oils, Aircraft Turbine Engine Lubricants, and Other Highly Refined Oils
D 4683	Standard Test Method for Measuring Viscosity at High Shear Rate and High Temperature by Tapered Bearing Simulator
D 4684	Standard Test Method for Determination of Yield Stress and Apparent Viscosity of Engine Oils at Low Temperature (MRV TP-1 Cycle)
D 4693	Standard Test Method for Low Temperature Torque of Grease-Lubricated Wheel Bearings
D 4739	Standard Test Method for Base Number Determination by Potentiometric Titration
D 4741	Standard Test Method for Measuring Viscosity at High Temperature and High Shear Rate by Tapered-Plug Viscometer
D 4742	Standard Test Method for Oxidation Stability of Gasoline Automotive Engine Oils by Thin-Film Oxygen Uptake (TFOUT)
D 4857	Standard Test Method for Determination of Coefficient of Friction of Lubricants Using the Four-Ball Wear Test Machine
D 4927	Standard Test Method for Elemental Analysis of Lubricant and Additive Components, Barium, Calcium, Phosphorus, Sulfur, and Zinc, by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy
D 4950	Standard Classification and Specification for Automotive Service Greases
D 4951	Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry
D 5119	Standard Test Method for Evaluation of Automotive Engine Oils in CRC L-38 Spark Ignition Engine

ASTM (Continued)

D 5133	Standard Test Method for Low Temperature, Low Shear Rate, Viscosity/ Temperature Dependence of Lubricating Oils Using a Temperature-Scanning Technique (Scanning Brookfield Test with Gelation Index Calculation)
D 5182	Standard Test Method for Evaluating the Scuffing Load Capacity of Oils (FZG Visual Method)
D 5183	Standard Test Method for Evaluating Coefficient of Friction of Lubricants Using the Four-Ball Wear Test Machine
D 5185	Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
D 5293	Standard Test Method for Apparent Viscosity of Engine Oils Between -5 and -30°C Using the Cold-Cranking Simulator
D 5302	Standard Test Method for Evaluation for Automotive Engine Oils in the Sequence VE Spark Ignition Engine
D 5480	Standard Test Method for Engine Oil Volatility by Gas Chromatography
D 5483	Standard Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry
D 5533	Standard Test Method for Evaluation of Automotive Engine Oils in the Sequence IIIE Spark Ignition Engine
D 5570	Standard Test Method for Evaluating the Thermal Stability of Manual Trans- mission Lubricants in a Cycle Durability Test
D 5621	Standard Test Method for Sonic Shear Stability of Hydraulic Fluids
D 5704	Standard Test Method for Evaluation of Thermal and Oxidative Stability of Lubricating Oils Used for Manual Transmissions and Final Drive Axles
D 5706	Standard Test Method for Determining Extreme-Pressure Properties of Lubri- cating Greases Using a High-Frequency, Linear-Oscillation (SRV) Test Machine
D 5707	Standard Test Method for Measuring Friction and Wear Properties of Lubricat- ing Grease Using a High Frequency, Linear-Oscillating (SRV) Test Machine
D 5800	Standard Test Method for Evaporation Loss of Lubricating Oils by the NOACK Method
D 5862	Standard Test Method for Evaluation of Engine Oils in Two-Stroke Cycle Turbo-Supercharged 6V92TA Diesel Engine
D 5864	Standard Test Method for Determining the Aerobic Aquatic Biodegradation of Lubricants or Their Components
D 5949	Standard Test Method for Pour Point of Petroleum Products
D 5969	Standard Test Method for Corrosion Preventive Properties of Lubricating Greases in the Presence of Dilute Synthetic Sea Water Environments
D 6006	Standard Guide for Assessing Biodegradability of Hydraulic Fluids
D 6022	Standard Test Method for Calculation of Permanent Shear Stability Index
D 6046	Standard Classification of Hydraulic Fluids for Environmental Impact
D 6081	Standard Practice for Aquatic Toxicity Testing of Lubricants: Sample Pre- paration and Results Interpretation
D 6082	Standard Test Method for High Temperature Foaming Characteristics of Lubricating Oils
D 6121	Standard Test Method for Evaluation of Load Carrying Capacity of Lubri- cants Under Conditions of Low Speed and High Torque Used for Final Hypoid Drive Axles

ASTM (Continued)

D 6138	Standard Test Method for Determination of Corrosion Preventive Properties of Lubricating Greases Under Dynamic Wet Conditions (Emcor Test)
D 6158	Standard Specification for Mineral Oil Hydraulic Oils
D 6186	Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)
D6278	Standard Test Method for Shear Stability of Polymer-Containing Fluids Using a European Diesel Injector Apparatus (see also D 3945)
D 6278	Standard Test Method for Shear Stability of Polymer Containing Fluids Using a European Diesel Injector Apparatus
D 6417	Standard Test Method for Estimation of Oil Volatility by Capillary Gas Chromatography
D 6425	Standard Test Method for Measuring Friction and Wear Properties of Extreme-Pressure (EP) Lubricating Oils Using SRV Test Machine
D 6557	Standard Test Method for Evaluation of Rust Preventative Characteristics of Automotive Engine Oils
D 6595	Standard Test Method for Determination of Wear Metals and Contaminants in Used Lubricating Oils or Used Hydraulic Fluids by Rotating Disk Electrode Atomic Emission Spectrometry
E 659	Standard Test Method for (1994)el Autoignition Temperature of Liquid Chemicals
E 1064	Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration
G133/95	Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear
STP 315H	Multicylinder Test Sequence for Evaluating Automotive Engine Oils
STP 509A	Single Cylinder Engine Test for Evaluating the Performance of Crankcase Lubricants

CEC Test Methods

L-01-A-79	Test for diesel engine crankcase oils using the Petter AV1 single cylinder laboratory diesel engine
L-02-A-78	Oil oxidation and bearing corrosion test using the Petter W1 single cylinder gasoline engine
L-07-A-85	Load carrying capacity test for transmission lubricants using the FZG test rig
L-11-T-72	The coefficient of friction of automatic transmission fluids using the DKA friction machine
L-12-A-76	Evaluation of piston cleanliness in the MWM KD 12 E test engine (Method B more severe)
L-14-A-93	Evaluation of the shear stability of lubricating oils containing polymers using the Bosch diesel fuel injector pump rig
L-18-A-80	Procedure for measurement of low temperature apparent viscosity by means of the Brookfield viscometer (liquid bath method)
L-19-T-77	Evaluation of the lubricity of two stroke engine oils (using the Motobecane engine AV7L 50 cm ³)
L-20-A-79	Evaluation of two stroke engine lubricants with respect to engine deposit formation oils (using the Motobecane engine AV7L 50 cm ³)

CEC Test Methods (Continued)

L-21-T-77	The evaluation of two stroke engine lubricants: Sequence I—Piston anti-seizure Sequence II—General performance Sequence III—Pre-ignition (using a Piaggio Vespa 180 SS engine)
L-24-A-78	Engine cleanliness under severe conditions using the Petter AVB supercharged diesel engine
L-25-A-78	Engine oil viscosity stability test (using a Peugeot 204 engine)
L-28-T-79	The evaluation of outboard engine lubricant performance (using Johnson and Evinrude marine outboard engines)
L-29-T-81	Ford Kent test procedure for evaluating the influence of the lubricating oil on piston ring sticking and deposit formation (using a Ford Kent engine)
L-30-T-81	Cam and tappet pitting test procedure (using MIRA cam and tappet test machine)
L-31-T-81	Predicting the borderline pumping temperature of engine oils using the Brookfield viscometer
L-33-A-94	Biodegradability of two-stroke cycle outboard engine oils in water
L-34-T-82	Pre-ignition tendencies of engine lubricants (using a Fiat 132C engine)
L-35-T-84	Motor oil evaluation in a turbocharged passenger car diesel engine (using a VW ATL 1.6 litre)
L-36-A-90	The measurement of lubricant dynamic viscosity under conditions of high shear (using a Ravensfield viscometer)
L-37-T-85	Shear stability test for polymer-containing oils (using the FZG test rig)
L-38-A-94	Valve train scuffing (using a PSA TU3 engine) wear test
L-39-T-87	Oil/elastomer compatibility test
L-40-A-93	Lubricating oil evaporative losses (using NOACK evaporative tester)
L-41-T-88	Evaluation of sludge-inhibition qualities of motor oils in a gasoline engine (using a Mercedes Benz M102E engine)
L-42-A-92	Evaluation of bore polish, piston cleanliness, liner wear and sludge in a DI turbo-charged diesel engine (using Mercedes Benz OM364A engine)
L-46-T-93	VW Intercooled turbo-Diesel ring stiching and Piston cleanliness test
L-51-T-95	OM 602A neon test
L-53-T-95	M111 black sludge test
L-55-T-95	TU3 MH high temperature deposits, ring stiching, oil thickening test
L-56-T-95	XUD11 ATE medium temperature dispensarity test

GM

9099P	Engine Oil Filterability Test (EOFT) (to be modified for GF-3)
-------	--

SAE

J183	Engine Oil Performance and Engine Service Classification (Other Than "Energy-Conserving")
J300	Engine Oil Viscosity Classification Standard
J357	Physical and Chemical Properties of Engine Oils
J1423	Classification of Energy-Conserving Engine Oil for Passenger Cars, Vans, and Light-Duty Trucks

Miscellaneous Test Methods

CEM Electric Motor Test (grease)				
DIN 51350 Part 2 Weld Load				
DIN 51350 Part 3 Wear Scar				
DIN 51802 (IP-220) Emcor Rust Test				
DIN 51851 (ASTM-D 5100 NOACK Volatility)				
Emcor Rust Test (grease)				
FE-8 Test (grease)				
FTM-350	Evaporation Loss			
FTM-791B	Cone Bleed			
FTM-791C	(Method 3470.1) Homogeneity and Miscibility			
FTM-3009	Contamination, Panicle (oils)			
FTM-3411	Thermal Stability and Corrosivity			
FTM-5309	Corrosion, Copper, 24 Hours			
FTM-5322	Corrosiveness (bimetallic couple)			
GE Electric Motor Test (grease)				
JPI-55-55-99 Hot Tube Test				
Mil-H-46170, Water Sensitivity				
Mil-H-83282, High-Temperature Stability (sealed ampule)				
SKF R2F Test (simulates paper mill applications)				
USS Low-Temperature Mobility Test (grease)				

Federal Supply Class 9150 Product Commodities

Document	Summarized title and description	QPL	Custodian	NATO code
MIL-PRF-23699F	Synthetic Aircraft Turbine Engine Oil	Yes	Navy/AS	O-156/O-154
MIL-PRF-23827C	Aircraft and Instrument Grease	Yes		G-354
MIL-PRF-81322F	Aircraft Wide Temperature Range Grease	Yes		G-395
MIL-PRF-81329D	Solid Film Lubricant	No(FAT)		S-1737
MIL-PRF-83282D	Synthetic Fire Resistant Hydraulic Fluid	Yes		H-537
MIL-PRF-85336B	All Weather Lubricant for Weapons	Yes		
MIL-L-19701B	Semi-Fluid Lubricant for Weapons	Yes		
MIL-G-21164D	Molybdenum Disulfide Grease	Yes		G-353

Federal Supply Class 9150 Product Commodities (Continued)

MIL-L-23398D	Solid Film Lubricant, Air-Cure	Yes		S-748
MIL-G-23549C	General Purpose Grease	Yes		
MIL-G-25013E	Aircraft Bearing Grease	Yes		G-372
MIL-G-25537C	Aircraft Helicopter Bearing Grease	Yes		G-366
MIL-H-81019D	Hydraulic Fluid for Ultra Low Temperatures	Yes		
MIL-S-81087C¹	Silicone Fluid	Yes		H-536
MIL-G-81827A	Aircraft High Loading and Anti-Wear Grease	Yes		
MIL-L-81846	Instrument Ball Bearing Lubricating Oil	No		
MIL-G-81937A	Ultra Clean Instrument Grease	Yes		
DOD-L-85645A¹	Dry Thin Film Lubricant	No		
DOD-G-85733	High Temperature Catapult Grease	Yes		
DOD-L-85734	Synthetic Helicopter Transmission Lubricant	Yes		
VV-D-1078B	Silicone Fluid Damping Fluid	No		S-1714 to 1732
SAE-J1899	Aircraft Piston Engine Oil, Ashless Dispersant	Yes		O-123/O-128
SAE-J1966	Aircraft Piston Engine Oil, Non Dispersant	Yes		O-113/O-117
SAE AMS-G-4343	Pneumatic Systems Grease	No		G-392
SAE AMS-G-6032	Plug Valve Grease	Yes		G-363
MIL-H-22072C	Hydraulic Fluid for Catapults	Yes	Navy/AS ²	H-579
A-A-59290	Arresting Gear Hydraulic Fluid	No	Navy/AS ²	
MIL-PRF-9000H	Diesel Engine Oil	Yes	Navy/SH	O-278
MIL-PRF-17331H	Steam Turbine Lubricating Oil	Yes		O-250
MIL-PRF-17672D	Hydraulic Fluid	Yes		H-573
MIL-PRF-24139A	Multipurpose Grease	Yes		
DOD-PRF-24574	Lubricating Fluid for Oxidizing Mixtures	Yes		
MIL-L-15719A	High Temperature Electrical Bearing Grease	Yes		
MIL-T-17128C	Transducer Fluid	No		
MIL-G-18458B	Exposed Gear and Rope Grease	Yes		
MIL-H-19457D	Fire Resistant Hydraulic Fluid	No(FAT)		H-580
MIL-L-24131B	Graphite and Alcohol Lubricant	Yes		
MIL-L-24478C	Molybdenum Disulfide and Alcohol Lubricant	No		

Federal Supply Class 9150 Product Commodities (Continued)

DOD-G-24508A	Multipurpose Grease	Yes		
DOD-G-24650	Food Processing Equipment Grease	No		
DOD-G-24651	Food Processing Equipment Lubricating Oil	No		
VV-L-825C	Lubricating Oil for Refrigerant Compressors	No		O-282/O-290
A-A-50433	Sea Water Resistant Grease	No		
A-A-50634	Lubricating Oil for Compressors Using HFC-134A	No		
A-A-59004A	Anti-Galling Compound	No		
MIL-PRF-6081D	Jet Engine Lubricating Oil	Yes	Air Force/11	O-132/O-133
MIL-PRF-6085D	Aircraft Instrument Lubricating Oil	Yes		O-147
MIL-PRF-6086E	Aircraft Gear Petroleum Lubricating Oil	Yes		O-153/O-155
MIL-PRF-7808L	Aircraft Turbine Synthetic Engine Oil	Yes		O-148/O-163
MIL-PRF-7870C	Low Temperature Lubricating Oil	Yes		O-142
MIL-PRF-8188D	Corrosion Preventive Engine Oil [FSC 6850]	Yes		C-638
MIL-PRF-27601C	Hydraulic Fluid	Yes		
MIL-PRF-27617F	Aircraft and Instrument Grease	Yes		G-397-399/-1350
MIL-PRF-32014	Aircraft and Missile High Speed Grease	No		
MIL-PRF-83261B	Aircraft Extreme Pressure Grease	No		
MIL-PRF-83363C	Helicopter Transmission Grease	No		G-396
MIL-PRF-87100A	Aircraft Turbine Synthetic Engine Oil	Yes		
MIL-PRF-87252C	Dielectric Coolant Fluid [FSC 9160]	Yes		S-1748
MIL-PRF-87257A	Synthetic Fire Resistant Hydraulic Fluid	Yes		H-538
MIL-H-5606G¹	Petroleum Hydraulic Fluid for Aircraft/Ordnance	Yes		H-515
DOD-L-25681D	Silicone Fluid with Molybdenum Disulfide	No	Air Force/68	S-1735
MIL-L-87177A	Synthetic Corrosion Preventive Lubricant	No(FAT)	Air Force/70	
MIL-PRF-2104G	Combat/Tactical Diesel Engine Oil	Yes	Army/AT	O-236/-237/-1236
MIL-PRF-2105E	Multipurpose Gear Oil	Yes		O-186/-226/-228

Federal Supply Class 9150 Product Commodities (Continued)

MIL-PRF-3150D	Preservative Oil	Yes		O-192
MIL-PRF-6083F	Operational and Preservative Hydraulic Fluid	Yes		C-635
MIL-PRF-10924G	Automotive/Artillery Grease	Yes		G-403
MIL-PRF-12070E	Fog Oil	No		F-62
MIL-PRF-21260E	Preservative and Break-in Engine Oil	Yes		C-640/C-642
MIL-PRF-32033	Preservative and Water-Displacing Oil	Yes		O-190
MIL-PRF-46002C	Vapor Corrosion Inhibitor (VCI) Preservative Oil	No(FAT)		
MIL-PRF-46010F	Solid Film Lubricant	Yes		S-1738
MIL-PRF-46147C	Solid Film Lubricant	Yes		
MIL-PRF-46167C	Arctic Engine Oil	Yes		O-183
MIL-PRF-46170C	Synthetic Fire Resistant Hydraulic Fluid	Yes		H-544
MIL-PRF-46176B	Silicon Brake Fluid	Yes		H-547
MIL-PRF-53074A	Steam Cylinder Lubricating Oil	No		O-258
MIL-PRF-53131A	Precision Bearing Synthetic Lubricating Oil	Yes		
VV-G-632B	General Purpose Industrial Grease	No		
VV-G-671F	Graphite Grease	No		G-412
A-A-52039B	Automotive Engine Oil API Service SH	No		
A-A-52036A	Commercial Heavy Duty Diesel Engine Oil	No		
A-A-59354	Hydraulic Fluid for Machines	No		
SAE J1703	Conventional Brake Fluid	No		H-542
MIL-PRF-63460D	Cleaner-Lubricant- Preservative for Weapons	Yes	Army/AR	S-758
MIL-L-11734C	Synthetic Lubricant for Mechanical Fuse Systems	No		
MIL-L-14107C	Low Temperature Weapons Lubricant	Yes		O-157
MIL-L-45983	Heat-Cured Solid Film Lubricant	No		
MIL-L-46000C	Semi-Fluid Weapons Lubricant	Yes		O-158
MIL-G-46003A	Rifle Grease	Yes		
MIL-L-46150	Semi-Fluid High Loading Weapons Lubricant	Yes		
MIL-PRF-3572B	Colloidal Graphite in Oil	No	DSCR/GS	
MIL-DTL-17111C	Power Transmission Fluid	No(FAT)		H-575
MIL-PRF-26087C	Reciprocating Compressor Lubricating Oil	No		

Federal Supply Class 9150 Product Commodities (Continued)

<i>MIL-L-3918A</i> ¹	Instrument Lubricating Oil for Jewel Bearings	No
<i>MIL-L-46014</i> ¹	Spindle Lubricating Oil	No
<i>MIL-L-83767B</i> ¹	Vacuum Pump Lubricating Oil	No
VV-C-846B	Emulsifiable Oil Type Cutting Fluids	No
A-A-50493A	Penetrating Oil	No
A-A-59113	Machine Tools/Slideways Lubricating Oil	No
A-A-59137	Breech Block Lubricating Oil (Naval Ordnance)	No
A-A-59173	Silicone Grease	No
A-A-59197	Fatty Oil for Metal Working Lubricants	No
SAE AS1241C	Fire Resistant Phosphate Ester Hydraulic Fluid	No

¹Those specifications in bold italics had been designated as "Inactive for New Design" and no longer used except for replacement purpose. Their QPLs will be maintained until the products are no longer required.

²See Navy/AS² under Abbreviations Used below.

Specifications Having Cross Reference Between, JIS, ASTM, and Others

ASTM or others	JIS	Title and contents
F 312	B 9930	Hydraulic Fluid—Determination of Particulate Contamination by the Particle Count Method
F313	B 9931	Fluid Contamination—Determination of Contaminants by the Gravimetric Method
D 117	C 2101	Testing method of electrical insulating oils
D 923		Sampling
D 4559		Evaporation
D 1218/21807		Refractive index and specific dispersion
D 974		Total acid number
D 1275		Corrosive sulfur
D 1533		Water content
D 2112/2440		Oxidation stability
D 877/1816		Dielectric strength
D 924		Dielectric loss tangent and relative dielectric constant
D 1169		Volume resistivity
	K 2249	Crude petroleum and petroleum products—Determination of the density and petroleum measurement tables based on a reference temperature (15°C)
D 1298/E100		I-shaped float method
D 4052/5002		Oscillating method
ISO 3833		Wardon picnometer method
D 941		I-shaped picnometer method
D 70		Hubbard picnometer method

Specifications Having Cross Reference Between, JIS, ASTM, and Others (Continued)

D 1250		Density, mass and volume conversion table
D 140/4057/4177	K 2251	Crude Petroleum and Petroleum Products—Sampling
D 1093	K 2252	Testing Method for Reaction of Petroleum Products
	K 2254	Petroleum products—Determination of distillation characteristics
D 86, E133		Test method for distillation of petroleum products at atmospheric pressure
D 1160		Test method for distillation of petroleum products at reduced pressure
D 2287		Test method for boiling range distillation of petroleum products by gas chromatography
	K 2255	Petroleum products—Gasoline—Determination of lead content
D 3341		Iodine monochloride method
D 3237		Atomic absorption spectroscopy method
D 661	K 2256	Testing Methods for Aniline Point and Mixed Aniline Point of Petroleum Products
D 323	K 2258	Testing Method for Vapor Pressure of Crude Oil and Petroleum Products (Reid Method)
D 381	K 2261	Petroleum products—Motor gasoline and aviation fuels—Determination of existent gum—Jet evaporation method
	K 2265	Crude oil and petroleum products—Determination of flash point
D 56		Tag closed test
D 3828/3278		Small scale closed test
D 93		Pensky-Martens closed cup test
D 92		Cleveland open cup test
	K 2269	Testing methods for pour point and cloud point of crude oil and petroleum products
D 97		Pour point
D 2500		Cloud point
	K 2270	Crude Petroleum and Petroleum products—Determination of carbon residue
D 189		Conradson method
D 4530		Micro method
	K 2272	Testing methods for ash and sulfated ash of crude oil and petroleum products
D 482		Ash
D 874		Sulfated ash
	K 2275	Crude oil and petroleum products—Determination of water content
D 95/4006		Distillation method
D 4377/1744		Karl-Fischer volumetric method
		Karl-Fischer coulometric method
DIN 9114		Hydride reaction method
	K 2276	Petroleum products—Testing methods for aviation fuels
D 873		Oxidation stability (potential residue)
D 2386		Freezing point

Specifications Having Cross Reference Between, JIS, ASTM, and Others (Continued)

D1094		Water tolerance
D 235/4952		Doctor test
D 3227		Determination of mercaptan sulfur (potentiometric method)
D 1740		Luminometer number test
D 1840		Determination of naphthalene (ultraviolet spectroscopy)
FS 1151.2		Explosive vapor test
D 3242		Total acid number
D 3948		Water separation index (micro separometer)
D 2550		Water separation index (water separometer)
D 3241		Thermal stability (JFTOT)
D 2276/5452		Particulate contaminant
IP 227		Copper corrosion
D 2624		Electric conductivity
D 3343		Hydrogen content
	K 2279	Crude petroleum and petroleum products—Determination and estimation of heat of combustion
D 4529/4868		Net heat of combustion
D 4868		Gross heat of combustion
	K 2280	Petroleum products—Fuels—Determination of octane number, cetane number and calculation of cetane index
D 2699		Research octane number
D 2700		Motor octane number
D 909		Supercharge octane number
D 613		Cetane number
D 4737		Calculation method for cetane index using four variable equation
D 1368		Small amount of lead in <i>n</i> -heptane and isooctane (dithizone method)
D 2268		Purity of <i>n</i> -heptane and isooctane (capillary gas chromatography)
	K 2283	Crude petroleum and petroleum products—Determination of kinematic viscosity and calculation of viscosity index from kinematic viscosity
D 445/446		Kinematic viscosity
D 2270		Viscosity index
D 341		Estimated relation between kinematic viscosity and Temperature
D 525	K 2287	Testing Methods for Oxidation Stability of Gasoline (Induction Period Method)
IP 309	K 2288	Gas oil—Determination of cold filter plugging point
	K 2301	Fuel gas and natural gas—Methods for chemical analysis and testing
D 1145		Sampling of gas sample
D 1945/1946		Chemical analysis (gas chromatography)
ISO 6326-1		Analysis of total sulfur
ISO 6326-1		Analysis of hydrogen sulfide
ISO 6327		Analysis of water (dew point method)
D 900/1826		Heat of combustion (Junkers gas calorimeter)

Specifications Having Cross Reference Between, JIS, ASTM, and Others (Continued)

D 3588		Heat of combustion (calculation method)
D 1070		Specific gravity (picnometer method)
D 3588		Specific gravity (calculation method)
D 4057	K 2420	Method of Sampling for Aromatic Hydrocarbon and Tar Products
	K 2501	Petroleum products and lubricants—Determination of neutralization number
D 974		Color indicator titration (TAN, strong acid number, strong base number)
D 664		Potentiometric titration (TAN, strong acid number)
D 4739		Potentiometric titration (TBN, strong base number)
D 2896		Potentiometer titration (TBN, perchloric acid method)
	K 2503	Testing method of lubricating oil for aircraft
D 91/2273		Precipitation number
D 94		Saponification number
FS 3006.3		Contamination
FS 204.1		Diluted pour point
ISO 6617		Oxidation stability
FS 5308.7		Corrosiveness and oxidation stability
D 665	K 2510	Testing Method for Rust-Preventing Characteristics of Lubricating Oil
D 130	K 2513	Petroleum Products—Corrosiveness to Copper—Copper Strip Test
	K 2514	Lubricating oils—Determination of oxidation stability
ISOT ¹		Oxidation stability of lubricants for internal combustion engine
D 943		Turbine oil oxidation stability test (TOST)
D 2272		Rotating pressure vessel oxidation test (RBOT)
D 3397		Total acid number (semimicro method)
IP 280		Turbine oil oxidation stability (oil soluble catalyst method)
D 892	K 2518	Petroleum products—Lubricating Oils—Determination of Foaming Characteristics
	K 2619	Lubricating oils—Testing methods for load carrying capacity
D 2619		Soda four ball (4 ball test modified by Dr. Soda)
D 2782		Timken
	K 2520	Petroleum products—Lubricating oils—Determination of demulsibility characteristics
D 1401		Demulsibility test
IP 19		Steam emulsion number
	K 2536	Liquid petroleum products—Testing method of components
D 1319/2001/2427		Fluorescent indicator adsorption analysis (FIA)
D 2267/4420/5580		Determination of aromatics by gas chromatography
D 1322	K 2537	Petroleum Product—Aviation Turbine Fuels and Kerosene—Determination of Smoke Point
	K 2540	Testing method for thermal stability of lubricating oils
	K 2541	Crude oil and petroleum products—Determination of sulfur content

specifications Having Cross Reference Between, JIS, ASTM, and Others (Continued)

D 2785/ISO 4260		Oxy-hydrogen combustion method
D 3120		Microcoulometric titration
D 1551		Quartz tube test
D 4294/ISO 8754		Energy dispersive x-ray fluorescence spectroscopy
D129		General bomb method
D 1266		Lamp method
D 2622		Wavelength dispersive x-ray fluorescence spectroscopy
	K 2580	Petroleum products—Determination of color
D 156		Saybolt
D 1500		ASTM
	K 2601	Testing methods for crude petroleum
D 3828		Flash point
D 96/4007/1796		Water and sediment
IP 77		Salt content (titration)
D 3230		Salt content (coulometric)
D 2892		Distillation at atmospheric pressure
D 1159/2710	K 2605	Petroleum distillates and commercial aliphatic olefins—Determination of bromine number—Electrometric method
	K 2609	Crude petroleum and petroleum products—Determination of nitrogen content
D 3228		Macro-Kjeldahl method
D 3431		Microcoulometric titration
D 4629/5762		Chemiluminescence method

Notes: •ISOT stands for Indiana Stirring Oxidation Test.

Abbreviations Used

QPL—Qualified Products Listing.

FAT—No QPL exists, but a First Article Test (FAT) is required or may be optional.

Navy/AS—Naval Air Systems Command (NAVAIR), Patuxent River, MD.

Navy/AS²—Naval Air Systems Command (NAVAIR), Lakehurst, NJ.

Navy/SH—Naval Sea Systems Command (NAVSEA), Arlington, VA.

Navy /YD—Naval Facilities Engineering Command (NAVFAC), Alexandria, VA.

Air Force/11—Air Force Aeronautical Systems Center (ASC), Wright-Patterson AFB, OH.

Air Force/68—Air Force San Antonio Air Logistics Center (SAALC), Kelly AFB, TX.

Air Force/70—Hill Air Force Base Logistics Center, UT.

Army/AT—Army Tank-Automotive and Armaments Command, Tank-Automotive Research Development and Engineering Center (TARDEC), Warren, MI.

Army/AR—Army Tank-Automotive and Armaments Command, Armaments Research Development and Engineering Center (ARDEC), Picatinny, NJ.

DSCR/GS—Defense Logistics Agency's Defense Supply Center Richmond (DSCR), Richmond, VA.

Acknowledgements

This chapter was compiled with the generous help of several colleagues in the lubricant community. The author thanks Piet Purmer (Shell Chemical Company), Dick Kuhlman (Ethyl Corporation), Don Campbell, Ed Zaweski, and Hiroshi Yamaoet (Amoco Chemicals—retired), Alan Plomer (BP—Belgium), Darryl Spivey (BP—Analytical), Ed Snyder (AFRL/MLBT), and Bob Rhodes.

Lubricant Industry Related Terms and Acronyms

LESLIE R. RUDNICK

*The Energy Institute, The Pennsylvania State University, University Park,
Pennsylvania, U.S.A*

The plethora of acronyms related to the field of lubrication continues to grow. These acronyms and abbreviations come from a variety of diverse industries and disciplines, including original equipment manufacturers, component suppliers, lubricant additive and fluid suppliers and producers, and professional societies directly and peripherally involved in the lubricants industry. Each class of lubricants, synthetic and conventional, has its set of abbreviations reserved to describe differences in structure or performance characteristics. Terms and acronyms for lubricant additives are numerous and generally reflect the chemical structure or type of additive. In some cases the acronym reflects the function of the additive. Acronyms created at different times by different industries have resulted in identical abbreviations that refer to different things.

This chapter collects in one place many of the important terms generally used in the lubricants industry. A complete list would require far more space than can be devoted in this book.

Terms and Acronyms

2T/2-cycle	term applied to lubricants for 2-cycle engines (i.e., motorcycles, outboard marine motors, weed whackers, etc.)
4T	a term applied to lubricants for four-cycle engines
AAMA	American Automobile Manufacturers Association
AAR	American Association of Railroads
AB	alkylbenzene

ABMA	American Bearing Manufacturers Association—a nonprofit association of American manufacturers of antifriction bearings, spherical plain bearings, or major components thereof. The purpose of ABMA is to define national and international standards for bearing products and maintain bearing industry statistics.
ABOT	Aluminum Beaker Oxidation Test for Ford Mercon ATF approval
ABSA	alkylbenzenesulfonic acid; precursor to overbased calcium sulfonate
ACC	American Chemistry Council
ACEA	Association des Constructeurs Européens d'Automobiles (European Auto Manufacturers Association)
ACIL	American Council of Independent Laboratories; ACIL is the national trade association representing independent, commercial engineering and scientific laboratory, testing, consulting and R&D firms.
ACS	American Chemical Society
additive	chemical compound or formulation of several chemical compounds added to a base oil to alter its physical, chemical, and/or performance properties
AFOA	American Fats and Oils Association
AFR	air/fuel ratio
AFNOR	Association Francaise de Normalisation
AFV	Alternate Fuel Vehicle
AGELFI	Cooperative Research Organization of AGIP, ELF, and FINA oil companies
AGMA	American Gear Manufacturers Association; an organization for the establishment and promotion of industrial gear lubricant standards
AGO	Automotive Gas Oil.
AHEM	Association of Hydraulic Equipment Manufacturers
AIAM	Association of International Automobile Manufacturers
AIChE	American Institute of Chemical Engineers
AIT	Autoignition temperature (ASTM D 2155), the lowest temperature at which a gas or vaporized liquid will ignite in the absence of an ignition source
ALTNER	Alternative Energy Programs of the European Commission
AMA	Automobile Manufacturers Association
ANFAVEA	Brazil Auto Manufacturers Association
ANIQ	Mexican equivalent to the CMA
ANSI	American National Standards Institute
Antioxidant	a chemical component added to lubricants to reduce the tendency for oxidation-related degradation of the oil
Antiwear additive	additives that can deposit multilayer films thick enough to supplement marginal hydrodynamic films and prevent asperity contact, or preferentially wear rather than allow contact between asperities that result in wear

AO	antioxidant
AOCA	American Oil Change Association; provides a link between the motoring public and auto maintenance specialists
AOCS	American oil Chemists Society; a global forum for the science and technology of fats, oils, surfactants, and related materials
APE	Association of Petroleum Engineers (U.S.A)
API	American Petroleum Institute; society organized to further the interest of the petroleum industry
API GL-4	designates the type of service characteristic of gears, particularly hypoid in passenger cars and other automotive-type equipment operated under high-speed, low-torque and low-speed, high-torque conditions; largely replaced by performance standard, API GL-5
API GL-5	designates the type of service characteristic of gears, particularly hypoid, in passenger cars and other automotive type equipment operated under high-speed, shock load; high-speed, low-torque; and low-speed, high-torque conditions.
AQIRP	Auto/Oil Air Quality Improvement Research Program
ARB	Air Resources Board (California)
ASA	American Soybean Association
ashless	additive containing no metallic elements
ASLE	American Society of Lubrication Engineers (now STLE)
ASM	automated manual transmission
ASM	American Society for Materials
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
A/T	conventional shifting automatic transmission
ATA	American Trucking Association
ATC	Additive Technical Council (European Petroleum Additive Industry Association, European CMA)
ATD	Allison Transmission Division; division of General Motors
ATF	Automatic Transmission Fluid
ATIEL	Association Technique de l' Industrie Européene des Lubrifiants (European Oil Marketers Association)
Auto-Oil-Program	a joint activity between the European Union (EU), the European Oil Industry (EUROPIA), and the European motor industry (ACEA)
AW	antiwear agent; minimizes wear by reacting with a metal surface to provide a protective layer.
BIA	Boating Industry Association; industry body organized to specify lubricants for marine application (now NMMA)
biodegradability	the ability of a chemical compound to be broken down by living organisms
BHRA	British Hydromechanics Research Association
BLF	British Lubricants Federation
Block grease	a very firm grease produced as a block that is applied to large open plain bearings that operate at low speed and high temperatures

BNA	Bureau des Normes de l'Automobile (France)
BNP	Bureau de Normalisation de Pétroles
BOCLE	ball on cylinder lubricity evaluator
BOFT	bearing oil film thickness
BOI	base oil interchange
BOTD	ball on three disks
Boundary lubrication	a regime of lubrication where there is partial contact between the metal components and partial separation of the surfaces by the lubricant fluid film
BPT	borderline pumping temperature (as defined in ASTM D 3829)
Br	bromine number (ASTM D 1158)
Brookfield viscosity	viscosity in centipoise, as determined on the Brookfield viscometer (ASTM D 2983) The operating principle for the Brookfield viscometer is the torque resistance on a spindle rotating in the fluid being tested. Although Brookfield viscosities are most frequently associated with low-temperature properties of gear oils and transmission fluids, they are in fact determined for many other types of lubricant.
BRT	ball rust test: the new bench test to replace Sequence IID engine test to measure rust and corrosion at low temperatures
BSFC	brake-specific fuel consumption
BSI	British Standards Institution
BTC	British Technical Council of the Motor and Petroleum Industries (CEC)
BTU	British Thermal Units
C-3	specification by Allison Division of General Motors covering transmission application
C-4	updated specification by Allison Division of General Motors covering transmission application
CA (API)	Service typical of diesel engines operated in mild to moderate duty with high-quality fuels and occasionally has included gasoline engines in mild service. Oils designed for this service provide protection from bearing corrosion and from ring belt deposits in some naturally aspirated diesel engines when using fuels of such quality that they impose no unusual requirements for wear and deposit protection. They were widely used in the late 1940s and 1950s but should not be used in any engine unless specifically recommended by the equipment manufacturer.
CAA	Clean Air Act
CAAA	Clean Air Act Amendment
CAFE	Corporate Average Fuel Economy
CARB	California Air Resources Board
carbon residue	percentage of coked material remaining after a sample of lubricating oil has been exposed to high temperatures under ASTM Method D 189 (Conradson) or D 524 (Ramsbottom)
Caterpillar 1P	a single-cylinder engine test designed to measure piston deposit control of an engine oil

CB(API)	Service typical of diesel engines operated in mild to moderate duty, but with lower-quality fuels that necessitate more protection for wear and deposits. Occasionally has included gasoline engines in mild service. Oils designed for this service provide necessary protection from bearing corrosion and from ring belt deposits in some naturally aspirated diesel engines with higher-sulfur fuels. Oils designed for this service were introduced in 1949.
CBOT	Chicago Board of Trade
CC(API)	Service typical of many naturally aspirated diesel engines operated in moderated to severe-duty service and certain heavy-duty gasoline engines. Oils designed for this service provide protection from high-temperature deposits and bearing corrosion and low-temperature deposits in gasoline engines. These oils were introduced in 1961.
CCD	combustion chamber deposits
CCMC	Comité des Constructeurs d'Automobiles du Marché Commun (Committee of Common Market Automobile Builders: precursor of ACEA)
CCPA	Canadian Chemical Producers Association
CCS	cold cranking simulator (ASTM D 5293)
CD (API)	Service typical of certain naturally aspirated, turbocharged, or supercharged diesel engines used when highly effective control of wear and deposits is vital or using fuels of a wide quality range including high-sulfur fuels. Oils designed for this service were introduced in 1955 and provide protection from bearing corrosion and from high-temperature deposits in these diesel engines. Oil meeting the performance requirements measured in the following diesel and gasoline engine tests: the 1-G2 diesel engine test has been correlated with indirect injection engines used in heavy-duty operation, particularly with regard to piston and ring groove deposits. The L-38 gasoline engine test requirement provides a measurement of copper-lead bearing weight loss and piston varnish under high-temperature operating conditions.
CD-II (API)	Service typical of two-stroke cycled engines requiring highly efficient control over wear and deposits. Oil designed for this service also meets all performance requirements of API service category CD. Oil meeting the performance requirements measured in the following diesel and gasoline engine tests: The 1-G2 diesel engine test has been correlated with indirect injection engines used in heavy-duty operation, particularly with regard to piston and ring groove deposits. The 6V-53T diesel engine test has been correlated with vehicles equipped with two-stroke cycle diesel engines in high-speed operation prior to 1985, particularly with regard to ring and liner distress. The L-38

	gasoline engine test requirement provides a measurement of copper/lead bearing weight loss and piston varnish under high-temperature operating conditions.
CE (API)	Service typical of many turbocharged or supercharged high-performance diesel engines, operated under both low-speed-high-load and high-speed/high-load conditions. Oils designed for this service have been available since 1984 and provide improved control of oil consumption, oil thickening, and piston assembly deposits and wear relative to the performance potential offered by oils designed for category CD service. Oil meeting the performance requirements of the following diesel and gasoline engine tests: the 1-G2 diesel engine test has been correlated with indirect injection engines used in heavy-duty service, particularly with regard to piston and ring groove deposits. The T-6, T-7, and NTC-400 are direct injection diesel engine tests. The T-6 has been correlated with vehicles equipped with engines used in high-speed operation prior to 1980, particularly with regard to deposits, oil consumption, and wear. The T-7 test has been correlated with vehicles equipped with engines used in lugging operation prior to 1984, particularly with regard to oil thickening. The NTC-400 diesel engine test has been correlated with vehicles equipped with engines in highway operation prior to 1983, particularly with regard to oil consumption, deposits, and wear. The L-38 gasoline engine test requirement provides a measurement of copper/lead bearing weight loss under high-temperature operating conditions.
CEC	California Energy Commission
CEC	Conseil Européen de Co-ordination pour les Développements des Essais de Performance des Lubrifiants et des Combustibles pour Moteurs (Coordinating European Council of Motor and Petroleum Industries: test standardization like ASTM)
CEE	Conseil Européen Economique
CEFIC	Conseil Européen des Federations de l'Industrie Chimique (European Chemical Industry Council)
CEN	European Standardization Council
CEN	Conseil Européen de Normalisation
CEPA	Canadian Environmental Protection Act
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CF (API)	API service category CF denotes service typical of indirect injected diesel engines, and other diesel engines that use a broad range of fuel types including those using fuel with higher-sulfur content (e.g., 0.5% wt.). Effective control of piston deposits, wear, and copper-containing bearing corrosion is essential for these engines, which may be naturally aspirated, turbocharged, or supercharged. Oils

	designated for this service have been in existence since 1994. Oils designated for this service may also be used when API service category CD is recommended.
CF-2 (API)	API service category CF-2 denotes service typical of two-stroke cycle engines requiring highly effective control over cylinder and ring-face scuffing and deposits. Oils designated for this service have been in existence since 1994 and may also be used when API Service Category CD-II is recommended. These oils do not necessarily meet the requirements of CF or CF-4 unless passing test requirements for these categories.
CF-4 (API)	This category was adopted in 1990 and describes oils for use in high-speed, four-stroke diesel engines. API CF-4 oils exceed the requirements of the CE category, providing improved control of oil consumption and piston deposits. <i>Oil meeting the performance requirements in the following diesel and gasoline engine tests:</i> The 1K diesel engine test, which has been correlated with direct injection engines used in heavy-duty service prior to 1990, particularly with regard to piston and ring groove deposits in the T-6, T-7, NTC-400, and L-38 engines: see API CE Category above for explanation.
CFPP	cold filter plugging point
CFR	Coordinating Fuel and Equipment Research Committee
CG	conventional gasoline
CG-4 (API)	API service category CG-4 describes oils for use in high-speed four-stroke cycle diesel engines used in both heavy-duty on-highway (less than 0.05% wt. sulphur fuel) and off-highway (less than 0.5% wt. sulfur fuel) applications. CG-4 oils provide effective control over high-temperature piston deposits, wear corrosion, foaming, oxidation stability, and soot accumulation. These oils are especially effective in engines designed to meet 1994 exhaust emission standards and may also be used in engines requiring API Service Categories CD, CE, and CF-4. Oils designated for this service have been in existence since 1994.
CGSB	Canadian General Standards Board; a consensus organization of producers, users, and general-interest groups that develops standards for test methods and products for Canada
CH-4 (PC-7)	new (proposed) classification for the generation of heavy-duty engine oils
CI	cetane index
CIA	Chemical Industries Association (part of the CEFIC)
CID1	compression ignition direct injection (diesel)
CIMAC	International Council on Combustion Engines
CLCA	Comité de Liaison de la Construction de l'Automobile
CLEPA	Comité de Liaison de la Construction d'Equipements et Pièces d'Automobiles
CLR	Cooperative Lubricants Research

CMA	Chemical Manufacturers Association; a standardizing body composed of additive manufacturers (U.S.)
CMAQ	Congestion Mitigation and Air Quality Improvement Program
CN	cetane number
CNG	compressed natural gas
CNPC	China National Petroleum Corporation
CO	carbon monoxide
CO ₂	carbon dioxide
CONCAWE	Conservation of Clean Air and Water (Europe)
Corrosion inhibitor	a lubricant additive used to protect surfaces against chemical attack from contaminants in the lubricating fluid or grease. These additives generally operate by reacting chemically and forming a film on the metal surfaces.
cP	centipoise = mPa · s (SI unit)
CPC	Chinese Petroleum Corporation
CPPI	Canadian Petroleum Product Institute
CRC	Coordinating Research Council; an American standardizing body for performance testing
cSt	centistokes
CSTCC	Continuously Slipping Torque Converter Clutch
Cummins M11	a heavy-duty engine test to measure crosshead wear
CUNA	Commission Technica di Unificazione Nel l'Autoveicolo (CEC)
CVMA	Canadian Vehicle Manufacturers Association
CVS	constant volume sampling
CVT	Continuously Variable Transmission
b-CVT	belt CVT
t-CVT	toroidal CVT
DAP	Detroit Advisory Panel (API)
DASMIN	Deutsche Akkreditierungastelle Mineralol (German)
DDC	Detroit Diesel Corporation
Demulsibility	a measure of the ability of an oil to separate from water as measured by the test time required for a specified oil–water emulsion to break using ASTM D 1401
DEO	diesel engine oil
DEOAP	Detroit Engine Oil Advisory Panel (API/EMA)
DETA	diethylene triamine
Detergent	oil additive that prevents deposits from forming on engine surfaces and may remove previously formed deposits
DEXRON®-II	General Motors trademark specification for ATF
DEXRON®-III	General Motors trademark specification for ATF, issued 1993
DEXRON®-IIIIG	General Motors trademark specification for ATF, issued 1998
DFA	diesel fuel additive
DGMK	Deutsche Gesellschaft fur Mineralölwissenschaft und Kohlechemie
DH-1	A JASO diesel engine oil category; a category mainly for Japanese-made heavy-duty diesel engines providing wear, soot-handling properties, and thermal-oxidative stability

DHYCA	Direction des Hydrocarbarres et Carburants (French Ministry of Industry)
DI	detergent inhibitor formulation direct injection (Normally Diesel) driveability index
DII	diesel injection improver
DIN	Deutsches Institut für Normung (German Standards Institute)
Dispersant	oil additive that keeps engines clean by holding in suspension the insoluble products for oil oxidation and fuel combustion formed during engine operation
DKA	Deutscher Koordmierungs-Ausschuss, the German National Body in the Coordinating European Council
DME	dimethyl ether
DNA	Deutsche Normenausschuss
DOA	dioctyl adipate
DOCP	dispersant olefin copolymer viscosity modifier or viscosity index improver
DOD	Department of Defense
DOE	Department of Energy
DOHC	double overhead cam
DOP	di 2-ethylhexylphthalate
DOS	di 2-ethylhexylsebacate
DOT	Department of Transportation (U.S.)
DPMA	Dispersant polymethacrylate viscosity modifier
Dropping point	the temperature at which a grease changes from a semisolid to a fluid under the test conditions. This temperature can be considered a measure of the upper use limit for the grease.
DSC	Differential Scanning Calorimetry—used to measure onset oxidation temperatures of oils
DTBP	di-tert-butyl phenol
DVM	Dispersant Viscosity Modifier
EC	European Community European Commission Environmental Council (Japan) energy conserving Environment Canada
EC-II (API)	Energy Conserving-II; designation that an engine oil provides 2.7% fuel economy improvement versus a reference oil in the Sequence VI test
ECCC	electronically controlled computer clutch
ECE	Economic Commission for Europe
ECTC	Engine Coolants Technical Committee (CEC)
EEB	European Environmental Bureau
EEC	European Economic Community Electronic Emission Controls
FELQMS	European Engine Lubricant Quality Management System
EFI	electronic fuel injection
EFTC	Engine Fuels Technical Committee (CEC)

EGR	exhaust gas recirculation
EHD	elastohydrodynamic (lubrication)
EHEDG	European Hygiene and Equipment Design Group
EIA	Energy Information Administration (U.S. DOE)
EINICS	European Inventory of Existing Chemical Substances
ELGI	European Lubricating Grease Institute
ELTC	Engine Lubricants Technical Committee (CEC)
EMA	Engine Manufacturers Association (U.S.); heavy-duty diesel
EMPA	Swiss Federal Laboratories for Materials Testing and Research
Emulsion	a mechanical mixture of two mutually insoluble fluids. Some metal-working fluids are designed to remain as a stable emulsion by incorporation of an emulsifier.
ENGVA	European Natural Gas Vehicle Association
EO-L	Mack Truck Company heavy-duty diesel specification, issued 1993
EO-J/EO-K/ EO-K/2	Mack Truck Company heavy-duty diesel specifications
EO-M	Mack Truck Company heavy-duty diesel specifications, issued 1998
EOFT	Engine Oil Filterability Test (GM)
EOLCS	Engine Oil Licensing and Certification System (API-1520)
EP additive	extreme pressure; an additive designed to prevent metal-metal adhesion or welding when the degree of surface contact is sufficiently high that the normal protective (oxide) films are removed and other surface-active species in the oil are not reactive enough to deposit a protective film. EP additives function by reacting with the metal surface to form a metal compound, e.g., iron sulfide.
EPA	Environmental Protection Agency (U.S.)
EPACT	Energy Policy Act
EPDM	ethylenepropylene diene-based elastomeric seal material
EPEFE	European Programme to Investigate Emissions from Fuels and Engines [an advisory group consisting of 14 motor companies (ACEA) and 32 oil companies (EUROPIA)]
EPM	ethylene propylene-based elastomeric seal material
ERC	European Registration Centre
ESCS	Engine Service Classification System
ESI	extended service, internal
ETC	European Transient Test Cycle
ETLP	Engine Tests of Lubricants Panel (IP)
EU	European Union
EUC	Elementary Urban Cycle
EUDC	Extra Urban Driving Cycle
EULIM	European Union of Independent Lubricant Manufacturers
EUROPIA	European Petroleum Industry Association
EV	electric vehicle
EVA	ethyl vinyl alcohol
FATG	Fuel Additive Task Group (CMA)

FBP	final boiling point
FCEV	fuel cell electric vehicle
FE	fuel economy
FEI	fuel economy improvement (fuel efficiency increase)
FERC	Federal Energy Regulatory Commission (U.S.)
FFV	flexible fuel vehicle
Fire point	ASTM D 92—a laboratory test to measure the lowest temperature at which a sample will sustain burning for five seconds
FISITA	Federation Internationale des Sociétés d'Ingenieurs des Techniques de l'Automobile
Flash point	ASTM D 92—a laboratory test to measure the tendency of a sample to form a flammable mixture with air, the lowest temperature at which a test flame causes the vapor of a fluid to ignite
Four Ball Test	Two test procedures based on the same principle: <ol style="list-style-type: none"> 1. Four-Ball EP Test (ASTM D 2596) 2. Four-Ball Wear Test (ASTM D 2266) <p>The three lower balls are clamped together to form a cradle upon which the fourth ball rotates in a vertical axis. The balls are immersed in the lubricant under investigation. The test is used to determine the relative wear-preventing properties of lubricants operating under boundary lubrication conditions. The test is carried out at a specified speed, temperature, and load. At the end of the specified period, the average diameter of wear scar on the three balls is reported. The Four-Ball EP Test is designed to evaluate performance under much higher loads. In this test, the top ball is rotated at a specified speed ($1700 \pm 60\text{rpm}$), but temperature is not controlled. The loading is increased at specified intervals until the rotating ball seizes and welds to the other balls. At the end of each interval the average scar diameter is recorded. Two values are generally reported—load wear index and weld point.</p>
FSIS	Food Safety Inspection Service
FTC	Federal Trade Commission (U.S.)
FTM	Federal Test Method (U.S.)
FTP	Federal Test Procedure (EPA)
FZG	Forschungstelle für Zahnrad und Getriebebau (Research Institute for Gears and Gearboxes)
GAO	General Accounting Office (U.S.)
GATC	gross additive treat cost
GC	gas chromatography
GC	In the ASTM D 4950 Standard Classification and Specification for Automotive Service Greases, the letters GC designate service typical of the lubrication of wheel bearings operating in passenger cars, trucks, and other vehicles under mild to severe duty.
GDI	gasoline direct injection
GDTC	gross delivered treating cost

GEO	gas engine oil; lubricant used for natural gas engines
GEPE	Group des Experts pour la Pollution et l'Énergie (Group of Experts for Pollution and Energy)
GF-2	ILSAC PCMO oil classification standard effective August 1997
GF-3	ILSAC PCMO oil classification after GF-2, proposed 2000
GFC	Groupe Française de Coordination (CEC)
GI	Gelation Index (as defined in ASTM D 5133)
GL-4/5	gear service characteristics (API)
GM	General Motors
GO-H	gear lubricant specified by Mack Truck Company
GRPE	Groupe des Rapporteurs pour la Pollution et l'Énergie
GSA	General Services Administration (U.S.)
HACCP	Hazard and Critical Control Point implement procedures for USDA regulators requirements
HC	hydrocarbon
HD	heavy duty
HDD	heavy-duty diesel
HDDEO	heavy-duty diesel engine oil
HDDO	heavy-duty diesel oil
HDEOCP	Heavy Duty Engine Oil Classification Panel
HEFCAD	high-energy, friction characteristics and durability; part of DEXRON®-II qualification program
HEUI	hydraulically operated electronically controlled unit injectors
HF-O	Denison specification for heavy-duty hydraulic antiwear fluids
HFRR	high-frequency reciprocating rig
HTHS	high-temperature, high-shear viscosity measured at 150°C and 10^6 s^{-1} (ASTM D 4683, CEC L-36-A-90) (ASTM D 4741), or ASTM D 5481)
HTHSRV	high-temperature, high shear rate viscosity
Hydrodynamic lubrication	a lubrication regime characterized by a full fluid film between two moving surfaces. As oil is moved between the moving parts, the action causes a high pressure in the lubricant fluid, and this separates the moving parts.
IBP	initial boiling point
ICOA	International Castor Oil Association
IchemE	Institution of Chemical Engineers (U.K.)
ICOMIA	International Council of Marine Industries Association
IDI	indirect injection (diesel)
IEA	International Energy Agency
IFP	Institut Français du Pétrole
IGL	Investigation Group Lubricants (CEC)
ILMA	Independent Lubricant Manufacturers Association; an association of oil companies also called compound-blenders
ILSAC	International Lubricant Standards Approval Committee
I/M	Vehicle Inspection and Maintenance Program
IMECHE	Institution of Mechanical Engineers
IOP	Institute of Physics—Tribology Group
IP	Institute of Petroleum (U.K.)

IR	infrared (spectroscopy)
ISO	International Standards Organization
ISOT	Indiana Stirred Oxidation Test (adopted as JIS K 2514)
ISTEA	Intermodel Surface Transportation Act
IVD	intake valve deposit
IVT	infinitely variable transmission
JALOS	Japanese Lubricating Oil Society
JAMA	Japan Automobile Manufacturers Association
JARI	Japan Automotive Research Institute
JASIC	Japan Automobile Standards Internationalization Centre
JASO	Japan Automotive Standards Organization
JUST	Japan Society of Tribologists
JATA	Japan Automobile Transport Technology Association
JCAP	Japan Clean Air Program
JD	John Deere; a farm implement manufacturer
JIC	J. I. Case; a farm implement manufacturer
JIS	Japan Industrial Standard
JISC	Japan Industrial Standards Committee
JPI	Japan Petroleum Institute
JSAE	Japan Society of Automotive Engineers
KTH	Royal Institute of Technology, Sweden
KV	kinematic viscosity
LB	In the ASTM D 4950 Standard Classification and Specification for Automotive Service Greases, the letters LB designate service typical of lubrication of chassis components and universal joints in passenger cars, trucks, and other vehicles under mild to severe duty.
LeRC	Lewis Research Center—NASA
LEV	low-emission vehicle
LMOA	Locomotive Maintenance Officers Association
LNG	liquefied natural gas
LOFI	Lubricant Oil Flow Improver
LPG	liquid petroleum gas
LRI	Lubricant Review Institute; a body associated with SAE that qualifies heavy-duty engine oil and gear lubricants for the industry and the U.S. military
LSC	Lubricant Standards Committee
LSD	low-sulfur diesel
Mack T-8	engine test used by Mack Truck Company in specifying heavy-duty diesel lubricants, extended to 300 hours
Mack T-9	engine test used by Mack Truck Company in specifying heavy-duty diesel lubricants, more severe (higher soot loading) test required for CH-4 specifications
M11	Cummins heavy-duty engine test (CH-4) to measure crosshead wear
M111	a Mercedes-Benz gasoline engine oil sludge test (CEC-L-53-T-95)
M111	a Mercedes-Benz gasoline engine oil fuel economy test (CEC-L-54-T-96)

Mannich	a name reaction that produces unique fuel and lubricant detergent/dispersants
MB	Mercedes-Benz
MB OM364A	a Mercedes-Benz heavy-duty diesel engine oil test to measure bore polish and piston cleanliness (CEC-L-42-A-92)
MB OM441LA	a Mercedes-Benz heavy-duty diesel engine oil test to measure bore polish, piston cleanliness, and turbo deposits (CEC-L-52-T-97)
MB OM602A	a Mercedes-Benz diesel engine oil test to measure cam wear (CEC-L-51-T-95)
MERCON [®] V	Ford Motor Company trademark ATF specification
MIL	Military Specification
MIL-L-2104F	latest in a series of heavy-duty diesel lubricants designated by the U.S. Military for over-the-road and off-highway applications
MIL-L-2105C	U.S. military specifications for mobile equipment gear lubricant, now superseded
MIL-L-2105D	U.S. military specification for mobile equipment gear lubricants; active through 1995
MIL-PRF-2105E	U.S. military gear specification, issued August 22, 1995
MIRA	Motor Industry Research Association (U.K.)
MITI	Ministry of International Trade and Industry (Japan)
MOD	Ministry of Defense
MOE	Ministry of Energy (U.K.)
MOFT	Minimum Oil Film Thickness
MOL	Ministry of Labor (Japan)
MON	motor octane number
MOT	Ministry of Transport (U.K.)
MOU	memorandum of understanding
MRV	minirotary viscometer—a measure of oil pumpability at various temperatures (ASTM D 3829 and ASTM D 4683)
MSDS	Material Safety Data Sheets
MT-1	manual transmissions specifications, issued 1995 (API)
MTAC	Multiple Test Acceptance Criteria
MTBE	methyl <i>t</i> -butyl ether
MTF	manual transmission fluid
MVEG	Motor Vehicle Emissions Group (Europe)
MVMA	Motor Vehicle Manufacturers Association (U.S. passenger cars)
MWF	metal-working fluid(s)
NA	Normally (or naturally) Aspirated (diesel engine)
NAAQS	National Ambient Air Quality Standards (U.S.)
NACE	National Association of Corrosion Engineers (U.S.)
NAEGA	North American Export Grain Association
NAFTA	North American Free Trade Agreement
NATC	net additive treat rate
NCM	National Comite Motorproeven (Netherlands) (CEC)
NCPA	National Cottonseed Products Association
NCWM	National Conference on Weights and Measures
NDOCP	nondispersant OCP

NDTC	net delivered treat rate
NDVM	nondispersant viscosity modifier
NEB	National Energy Board (NA) National Environmental Board (Thailand)
NEDO	New Energy and Technology Development Organization (Japan)
NEFI	New England Fuel Institute
NEL	National Engineering Laboratory (U.K.)
NESCAUM	Northeast States for Coordinated Air Use Management
NFPA	National Fluid Power Association
NGEO	Natural Gas Engine Oil
NGFA	National Grain and Feed Association
NIOP	National Institute of Oilseed Products
NIST	National Institute of Standards and Technology (U.S.)
NLEV	national low-emission vehicle
NLGI	National Lubricating Grease Institute (U.S.)
NMHC	nonmethane hydrocarbons
NMMA	National Marine Manufacturers Association (U.S.) [formerly Boating Industry Association (BIA)]
NMOG	Nonmethane organic gases (includes alcohols)
NOACK	NOACK volatility; DIN 51851 (ASTM D 5800)
NOPA	National Oilseed Processors Association
NORA	National Oil Recyclers Association (U.S.)
NOX	nitrogen oxides
NPA	National Petroleum Association (U.S.)
NPRA	National Petroleum Refiners Association (U.S.)
NRC	Natural Resources Canada
NRCC	National Research Council of Canada
NRL	Naval Research Laboratory
NTC-400	Cummins diesel engine test
NUTEK	Swedish National Board for Industrial and Technical Develop- ment
OCP	olefin copolymer viscosity modifier or viscosity index improver
ODI	oil drain interval
OEM	original equipment manufacturer (e.g., GM, Ford, etc.)
OICA	Organization Internationale des Constructeurs d'Automobiles (was BPICA)
OMB	Office of Management and Budget (U.S.)
OMS	Office of Mobile Sources (U.S. EPA)
ON	octane number
OPEST	Oil Protection of Emission Systems Test
ORD	octane requirement decrease
ORD	Office of Research and Development (U.S. EPA)
ORI	octane requirement increase
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration (U.S.)
OTA	Office of Technology Assessment (U.S.)
OTAG	Ozone Transport Assessment Group

OTC	Ozone Transport Commission
Oxidation	one of several modes of oil degradation. The process generally involves the addition of oxygen to the lubricant structure, followed by cleavage or polymerization, resulting in unfavorable oil properties and performance.
package	formulation of various chemical compounds
PADD	Petroleum Administration for Defense District
PAG	poly alkene glycols, polyalkylene glycols
PAH	polyaromatic hydrocarbons
PAJ	Petroleum Association of Japan
PAO	polyalphaolefin base stocks of various viscosity classifications
PAPTG	Product Approval Protocol Task Group (CMA)
PC	proposed classification
PCD	passenger car diesel
PCMO	Passenger Car Motor Oil
PDVSA	Petroleos de Venezuela
PEA	polyether amine
PFPE	perfluoropolyether
Phenolic	antioxidant based on 2,6-di- <i>tert</i> -butyl phenol chemistry or other alkylated phenolics
PIB	polyisobutene
PIBSA	polyisobutenyl succinic anhydride; precursor for ashless dispersants
PM	particulate matter
PM2.5	particulate matter less than 2.5- μ m diameter
PM10	particulate matter less than 10- μ m diameter
PMA	polymethacrylate viscosity index improver or viscosity modifier
PMAA	Petroleum Marketers Association of America
PMC	Pensky-Martin Closed Cup—flash point test
PNA	polynuclear aromatic
PNGV	Partnership for a New Generation of Vehicles (U.S.)
Poise	the CGS unit of absolute viscosity ($\text{dyne-sec}/\text{cm}^2$) as measured by the shear stress required to move one layer of fluid along another over a total thickness of 1 cm at a shear rate of 1 cm/sec. Absolute viscosity values are independent of density and are directly related to the resistance to flow.
pour point	This widely used low-temperature flow indicator and is 3°C above the temperature to which a normally liquid petroleum product maintains fluidity. It is a significant factor in cold-weather start-up, but must be considered along with pumpability, the ease with which an oil forms a honeycomb or crystals at low temperatures near the pour point. A conventional measure of the lower temperature limit for low-temperature flow of a lubricating fluid.
PPD	pour point depressant; an additive used to lower the pour point of an oil by modifying the structure of wax crystals
ppm	parts per million

PSA TU3M	a Peugeot gasoline engine test to measure cam wear and scuffing (CEC-L-38-A-94)
PSA TU3M	a Peugeot gasoline engine test to measure high-temperature ring sticking and piston varnish (CEC-L-55-T-95)
PSA XUD 11 ATE/BTE	a Peugeot diesel engine test to measure medium-temperature dispersivity (soot-induced oil thickening) (CEC-L-56-T-95)
PTIT	Petroleum Institute of Thailand
PTT	Petroleum Authority of Thailand
QPL	Qualified Products List (U.S. Military)
RBOT	rotating bomb oxidation test
RFG	reformulated gasoline
RI	Radial isoprene (star polymer) viscosity modifier or viscosity index improver
RME	rapeseed methyl ester
R&O	rust and oxidation; inhibited lubricant for use in circulating systems, compressors, hydraulic systems, and gear cases
RON	research octane number
ROSE	Rose Foundation—Recovery of Oil Saves the Environment
RSI	Registration Systems, Inc. (CMA monitoring agency)
rust inhibitor	a lubricant additive for protecting ferrous (iron and steel) components from rusting caused by water contamination or other harmful materials formed by oil degradation. Some rust inhibitors operate similarly to corrosion inhibitors by reacting chemically to form an inert film on metal surfaces. Other rust inhibitors absorb water by incorporating it into a water-in-oil emulsion so that only the oil touches the metal surfaces.
RVP	Reid vapor pressure
SA (API)	service typical of older engines operated under such mild conditions that the protection afforded by compounded oils is not required. This category should not be used in any engine unless specifically recommended by the equipment manufacturer.
SAE	Society of Automotive Engineers
SAIT	South African Institute of Tribologists
SB	Styrene-butadiene viscosity modifier or viscosity index improver
SB (API)	Service typical of older gasoline engines operated under such mild conditions that only minimum protection afforded by compounding is desired. Oils designed for this service have been used since the 1930s and provide only antiscaff capability and resistance to oil oxidation and bearing corrosion. They should not be used in any engine unless specifically recommended by the equipment manufacturer.
SC (API)	Service typical of gasoline engines in 1964 through 1967 models of passenger cars and some trucks operating under engine manufacturers' warranties in effect during those model years. Oils designed for this service provide control of high-and

	low-temperature deposits, wear, rust, and corrosion in gasoline engines.
SCAQM	South Coast [California] Air Quality Management
Scuffing	wear caused by the localized welding and fracture of rubbing surfaces
SD (API)	Service typical of gasoline engines in 1968–1970 models of passenger cars and some trucks operating under engine manufacturers' warranties in effect during those model years. Also may apply to certain 1971 and/or later models as specified (or recommended) in the owners' manuals. Oils designed for this service provide more protection against high- and low-temperature engine deposits, wear, rust, and corrosion in gasoline engines than oils that are satisfactory for API engine service category SC and may be used when API engine service category SC is recommended.
SE (API)	service typical of gasoline engines in passenger cars and some trucks beginning with 1972 and certain 1971 models operating under engine manufacturers' warranties. Oils designed for this service provide more protection against oil oxidation, high-temperature engine deposits, rust and corrosion in gasoline engines than oils which are satisfactory for API Engine Service Categories SD or SC and may be used when either of these classifications is recommended.
Sequence IIIE, F	engine test to simulate expressway driving to measure oxidation and wear characteristics of formulated oils at high temperature
Sequence tests	a series of (ASTM) industry standardized tests used to determine the quality of crankcase lubricants (i.e., Sequence IID, IIIE, VE, VIA)
Sequence VE, F	engine test to simulate stop-and-go driving and to measure sludge, varnish, cam wear, and oil screen plugging
Sequence VIA, B	engine test designed to measure fuel efficiency properties of an engine oil (VIA for ILSAC GF-2, VIB for ILSAC GF-3)
Sequence UL-38	engine test similar to L-38 except fuel used is unleaded; test measures bearing wear and deposits
SF (API)	service typical of gasoline engines in passenger cars and some trucks beginning with the 1980 model year operating under manufacturers' recommended maintenance procedures. Oils developed for this service provide increased oxidation stability and improved antiwear performance relative to oils that meet the minimum requirements for API service category SE. The oils also provide protection against engine deposits, rust, and corrosion. Oils meeting API service classification SF may be used where API service categories SE, SD, or SC are recommended.
	<i>Oil meeting the performance requirements measured in the following gasoline engine tests: the IID gasoline engine test has been correlated with vehicles used in short-trip service prior to</i>

1978, particularly with regard to rusting. The IID gasoline engine test has been correlated with vehicles used in high-temperature service prior to 1978, particularly with regard to oil thickening and valve train wear. The VD gasoline engine test has been correlated with vehicles used in stop-and-go service prior to 1978, particularly with regard to varnish, sludge, and valve train wear. The L-38 gasoline engine test requirement provides a measurement of copper/lead bearing weight loss under high-temperature operating conditions.

SG (API) service typical of gasoline engines in passenger cars, vans, and light trucks beginning with the 1989 model year operating under manufacturers' recommended maintenance procedures. Category SG quality oils include the performance properties of API service category CC. (Certain manufacturers of gasoline engines require oils also meeting API service category CD.)

Oils developed for this service provide improved control of engine deposits, oil oxidation, and engine wear relative to oils developed for previous categories. These oils also provide protection against rust and corrosion. Oils meeting API service category SG may be used where API service categories SF, SF/CC, SE, or SE/CC are recommended.

Oil meeting the performance requirements measured in the following gasoline and diesel engine tests: the IID gasoline engine test has been correlated with vehicles used in short-trip service prior to 1978, particularly with regard to rusting. The IIIE gasoline engine test has been correlated with vehicles used in high-temperature service prior to 1988, particularly with regard to oil thickening and valve train wear. The VE gasoline engine test has been correlated with vehicles used in stop-and-go service prior to 1988, particularly with regard to sludge and valve train wear. The L-38 gasoline engine test requirement provides a measurement of copper-lead bearing weight loss and piston varnish under high-temperature operating conditions. The 1-H2 diesel engine test requirement provides a measurement of high-temperature deposits.

SH (API) service requirement for gasoline engines and dated in 1993 for use in current and earlier passenger car, van, and light truck operation under vehicle manufacturers' recommended maintenance procedures.

Oils developed for this category may be used where SG oils are recommended. SH oils provide improved control of engine deposits, oil oxidation, wear, corrosion, and rust relative to oils developed for previous categories.

Engine oils that meet SH designation may use the API Base Oil Interchangeability Guidelines and API Guidelines for SAE Viscosity-Grade Engine Testing.

SHPDO	Super High-Performance Diesel oil
SI	styrene-isoprene viscosity modifier or viscosity index improver spark ignition
	Système Internationale—units of measurement (m, kg, sec, deg K)
SIA	Société des Ignenieurs de l'Automobile
SIB	sulfurized isobutylene; a basic extreme-pressure additive for gear lubricant packages
SIGMA	Society of Independent Gasoline Marketers of America
SIP	styrene–isoprene copolymer
SIP(s)	State Implementation Plan(s)
SIS	Sveriges Standardiseringskommission
SJ (API)	Service requirement adopted for gasoline engines in 1996 for use in current and earlier passenger car, sport utility vehicle, van, and light truck under vehicle manufacturers' recommended maintenance procedures. Oils developed for the category may be used where API SH and earlier categories are recommended. Engine oils that meet the category may use the API Base Oil Interchangeability Guidelines and the API Guidelines for SAE Viscosity-Grade Engine Testing.
SME	Society of Manufacturing Engineers
SMM&T	Society of Motor Manufacturers and Traders Ltd. (U.K.)
SMR	Svenska Mekanisters Riksforenig (National Organization in Sweden (CEC))
SMRP	Society for Maintenance and Reliability Professionals
SNPRM	supplemental notice of proposed rule making
SNV	Schweizerische Normenvereinigung (National Organisation, Switzerland) (CEC)
SOF	soluble oil fraction
SSI	shear stability index
SSU or SUS	Saybolt second universal or Saybolt universal second; a measure of viscosity, or a fluid's resistance to flow
STLE	Society of Tribologists and Lubrication Engineers
STOU	super tractor oil universal; a term commonly applied to a lubri- cant that can be used for all applications of a tractor, includ- ing hydraulic, engine, wet brakes, and gear
T-8	engine test used by Mack Truck Company in specifying heavy- duty diesel lubricants, extended to 300 hours
T-9	engine test used by Mack Truck Comapny in specifying heavy- duty diesel lubricants, more severe (higher soot loading) test required for CH-4 specifications
TAD	Technische Vereinigung fur Mineralöladitive in Deutschland EV (subgroup of the ATC)
TAN	Total acid number; a measure of a lubricant's acidity
TBN	Total base number; a measure of the acid-neutralizing property- of a lubricating oil
TBS	tapered bearing simulator (ASTM D 4683)

TCW-3	water-cooled two-cycle engine oil specification
TEOST	Thermal Engine Oil Stability Test
TFB	Swedish Transport Research Board
TFOUT	thin-film oxidation test
THCT	turbo hydramatic cycling test; part of DEXRON® qualification program
THOT	turbo hydramatic oxidation test; part of DEXRON® qualification program
TISI	Thailand Industrial Standards Institute
TLTC	Transmission Lubricants Technical Committee (of CEC)
Timken OK load	This is a measure of the extreme-pressure properties of a lubricant. Lubricated by the product under investigation, a standard steel roller rotates against a block. Timken OK load is the heaviest load that can be carried without scoring.
TMC	ASTM Test Monitoring Center
TO-2	Caterpillar specification for transmission oil, including durability and frictional property testing
TO-3	Caterpillar specification, including TO-2 plus fluoroelastomer seal compatibility
TO-4	Caterpillar specification, including TO-2 plus fluoroelastomer seal compatibility, nearest version of Caterpillar transmission and drive train fluid requirements
TOST	turbine oil stability test
TOU	Tractor Oil Universal; an oil that goes in all parts of the tractor, except for the engine
Tribology	the science and technology of interacting surfaces in relative motion and the practices related thereto
TSCA	Toxic Substances Control Act
TÜV	Technischer Überwachungs Verein
TVMD	see TAD
UDC	Urban Driving Cycle (Europe)
UEIL	Union Européen des Independants en Lubrifiants (European Union of Independent Lubricant Manufacturers)
UIC	Union des Industries Chimiques
UFIP	Union Française des Industries Petrolières
UKPIA	United Kingdom Petroleum Industry Association
ULEV	ultralow emission vehicle
USB	United Soybean Board
USCAR	United States Council for Automotive Research
USDA	United States Department of Agriculture
USX	formerly U.S. Steel; dominant maker of steel and specifier of industrial lubricants for the steel, and related, industries
UTAC	L'Union Technique de l'Automobile; du Motorcycle et du Cycle
UTTO	Universal Tractor Transmission Oil; used in all lubricating places, except the crankcase on a farm tractor
VCI	Verein der Chemischen Industrie
VDA	Verband der Automobilindustrie
VDI	Verein Deutscher Ingenieure

VDS, VDS2	Volvo Long Drain Lubricant Specification
VGRA	viscosity-grade read across
VI	viscosity index; a measure of the rate of change in viscosity with temperature (higher VI means less change) (ASTM D 2270)
VII	viscosity index improver; additive that increases the viscosity index beyond that which can be obtained using ordinary refining methods
Viscosity	measure of resistance of flow of a liquid; dynamic viscosity is the ratio between the applied shear and the rate of shear, expressed in poise or centipoise; kinematic viscosity is the ratio of the viscosity (dynamic viscosity) and the density of the liquid, expressed in stokes or centistokes
Viton®	a fluoroelastomeric compound from DuPont, presently used by Caterpillar and Mercedes-Benz for use in transmission application
VM	viscosity modifier
VMI	Viscosity Modifier Interchange
VOC	volatile organic compound
VOF	volatile organic fraction
Volatility	a measure of the amount of material evaporated from a sample under a particular set of conditions, usually expressed as a percentage of the original sample
VW DI	a Volkswagen direct injection diesel engine oil test to measure ring sticking and piston cleanliness (CEC-L-78-T-97)
VW 1431 TCIC	a Volkswagen indirect injection diesel engine oil test to measure ring sticking and piston cleanliness (CEC-L-46-T-93)
WASA	wax antisetling additive
WAFI	wax antisetling flow improver
WCM	wax crystal modifier
WSPA	Western States Petroleum Association
ZEVs	zero-emission vehicles
ZDDP	zinc dialkyldithiophosphate; a widely used antiwear and antioxidant agent for motor oils and industrial fluids; also referred to as ZDTP, ZDP, and “zinc”
ZF	German transmission manufacturer, Zahnradfabrik Friedrichshafen A.G.

Some Federal Supply Chain Abbreviations

QPL	Qualified Products Listing
FAT	No QPL exists, but a first article test (FAT) is required, or may be optional
Navy/AS	Naval Air Systems Command (NAVAIR), Patuxent River, MD
Navy/AS ²	Naval Air Systems Command (NAVAIR), Lakehurst, NJ
Navy/SH	Naval Sea Systems Command (NAVSEA), Arlington, VA
Navy /YD	Naval Facilities Engineering Command (NAVFAC), Alexandria, VA

Air Force/11	Air Force Aeronautical Systems Center (ASC), Wright-Patterson AFB, OH
Air Force/68	Air Force San Antonio Air Logistics Center (SAALC), Kelly AFB, TX
Air Force/70	Hill Air Force Base Logistics Center, UT
Army/AT	Army Tank-Automotive and Armaments Command, Tank-Automotive Research Development and Engineering Center (TARDEC), Warren, MI
Army/AR	Army Tank-Automotive and Armaments Command, Armaments Research Development and Engineering Center (ARDEC), Picatinny, NJ
DSCR/GS	Defense Logistics Agency's Defense Supply Center Richmond (DSCR), Richmond, VA

Internet Resources for the Lubricant Industry

LESLIE R. RUDNICK

*The Energy Institute, The Pennsylvania State University, University Park,
Pennsylvania, U.S.A.*

The Internet continues to become the repository of information of enormous breadth. Individuals, companies, universities, and the government are continuously contributing information that becomes the shared learning we strive for in this era of information.

This chapter is designed to be a collection of Internet sites that will be useful to the readership for which this book is directed. It should provide a ready reference to the main sites available at the time of its writing from government agencies, universities, and companies around the world that are directly involved in the production or marketing of lubricant fluids and additives, and other components of lubricating systems. Manufacturers of lubrication-related equipment have also been included.

Within many of the Internet sites listed for companies, you will find contact information such as company addresses and telephone and fax numbers. In addition, some companies have product lines listed with specifications and material safety data sheets (MSDS). Some companies list emergency contact numbers in the event of a spill or personal contact with one of their products. Several companies produce an online infomercial that contains technical information or performance testing results of their products. What you find depends on where you look and when. One advantage of the Internet is the wealth of information available. However, one disadvantage is that sites change so that information found today may not be there the next time the site is viewed. In fact, the site may not be there at all.

Government sites and organization sites list available publications, test methods, safety, health, environmental, and regulatory information. Information can also be obtained directly from various sites online, by mail, or by fax-back.

A variety of oil and fuel distribution companies have been included. Many researchers need to access supplies of finished lubricants and raw materials for comparative evaluations in their own laboratories. Analytical and engine test laboratories are also a part of this database of URLs.

In an effort of this type, there are always possibilities for omissions. Also, company name changes, mergers, and closings will affect the accuracy of a list of this type. The editor takes full responsibility for any errors that may have occurred in the preparation of this resource. All URLs were "hit" just prior to submission of this manuscript to check that every site was active, valid, or under construction.

This chapter has been prepared to be included as printed text within the book and to be included in CD format along with the book. This serves to maintain the chapter as an integral part of the manuscript and at the same time eliminate the need to type a URL to access the Web site. The CD format allows direct "link" to the site.

ALPHABETICAL LISTING

2V Industries Inc. www.2vindustries.com
49 North www.49northlubricants.com
76 Lubricants Company www.tosco.com
A.W. Chesterton Company www.chesterton.com
A/R Packaging Corporation www.arpackaging.com
Acculube www.acculube.com
Accumetric LLC www.accumetric.com
Accurate Lubricants & Metalworking Fluids Inc. (dba Acculube)
www.acculube.com
Acheson Colloids Company www.achesonindustries.com
Acme Refining, Division of Mar-Mor, Inc. www.acmerefining.com
Acme-Hardesty Company www.acme-hardesty.com
Adco Petrol Katkiları San Ve. Tic. AS www.adco.com.tr
Advanced Ceramics Corporation www.advceramics.com
Advanced Lubrication Technology, Inc. (ALT) www.altboron.com
Aerospace Lubricants, Inc. www.aerospacelubricants.com
AFD Technologies www.afdt.com
African Lubricants Industry www.mbendi.co.za/aflu.htm
AG Fluoropolymers USA, Inc. www.fluoropolymers.com
Airflow Systems, Inc. www.airflowsystems.com
Airosol Company, Inc. www.airosol.com
Akzo Nobel www.akzonobel.com
Alco-Metalube Company www.alco-metalube.com
Alfa Laval Separation www.alfalaval.com
Alfa Romeo www.alfaromeo.com
Alithicon Lubricants, Division of Southeast Oil & Grease
Company, Inc. www.alithicon.com
Allegheny Petroleum Products Company www.oils.com

Allen Filters, Inc. www.allenfilters.com
Allen Oil Company www.allenoil.com
Allied Oil & Supply, Inc. www.allied-oil.com
Allied Washoe www.alliedwasboe.com
Alpha Grease & Oil, Inc. www.alphagrease.thomasregister.com/olc/alphagrease/
ALT Inc. www.altboron.com
Amalie Oil Company www.amalie.com
Amber Division of Nidera, Inc. www.nidera-us.com
Amcar Inc. www.amcarinc.com
Amerada Hess Corporation www.hess.com
American Agip Company, Inc. www.americanagip.com
American Bearing Manufacturers Association www.abma-dc.org
American Board of Industrial Hygiene www.abih.org
American Carbon Society www.americancarbonsociety.org
American Chemical Society (ACS) www.acs.org
American Council of Independent Laboratories (ACIL) www.acil.org
American Eagle Technologies Inc. www.frictionrelief.com
American Gear Manufacturers Association (AGMA) www.agma.org
American International Chemical www.aicma.com/
American Lubricants Inc. www.americanlubricantsbflo.com
American Lubricating Company www.alcooil.com
American Machinist www.penton.com/cgi-bin/superdirectory/details.pl?id=317
American National Standards Institute (ANSI) www.ansi.org
American Oil & Supply Company www.aosco.com
American Oil Chemists Society (AOCS) www.aocs.org
American Petroleum Institute (API) www.api.org
American Petroleum Products www.americanpetroleum.com
American Refining Group Inc. www.amref.com
American Society for Testing and Materials (ASTM) www.astm.org
American Society of Mechanical Engineers International (ASME) www.asme.org
American Synthol Inc. www.americansynthol.com
Amoco www.amoco.com
Amtron Corporation www.superslipperystuff.com/organisation.htm
Amrep Inc. www.amrep.com
AMSOIL Inc. www.amsoil.com
Ana Laboratories Inc. www.analaboratories.com
Analysts Inc. www.analystinc.com
Anderol Specialty Lubricants www.anderol.com
Andpak Inc. www.andpak.com
ANGUS Chemical Company www.dowchemical.com
Anti Wear 1 www.dynamicdevelopment.com
API Links www.api.org/links
Apollo America Corporation www.apolloamerica.com
Applied Energy Company www.appliedenergyco.com
Aral International www.Aral.com

Arch Chemicals, Inc. www.archbiocides.com
ARCO www.arco.com
Argonne National Laboratory www.et.anl.gov
Arizona Chemical www.arizonachemical.com
Asbury Carbons, Inc.—Dixon Lubricants www.asbury.com,
www.dixonlube.com
Asbury Graphite Mills Inc. www.asbury.com
Asheville Oil Company, Inc. www.ashevilleoil.com
Ashia Denka www.adk.co.jp/eng.htm
Ashland Chemical www.ashchem.com
Ashland Distribution Company www.ashland.com
Asian Oil Company www.nilagems.com/asianoil/
Aspen Chemical Company www.aspenchemical.com
Aspen Technology www.aspentech.com/
Associated Petroleum Products www.associatedpetroleum.com
Associates of Cape Cod Inc. www.acciusa.com
ASTM www.astm.org
Atlantis International Inc. www.atlantis-usa.com
Atlas Oil Company www.atlasoil.com
ATOFINA Canada Inc. www.atofinacanada.com
Audi www.audi.com
Ausimont www.ausiusa.com
Automotive & Industrial Lubricants Guide www.wearcheck.com
Automotive Aftermarket Industry Association (AAIA) www.aftermarket.org
Automotive & Industrial Lubricants Guide by David Bradbury
www.escape.ca/~dbrad/index.htm
Automotive and Industrial Lubricants Tutorial [www.escape.ca/~dbrad/](http://www.escape.ca/~dbrad/index.htm)
[index.htm](http://www.escape.ca/~dbrad/index.htm)
Automotive News www.autonews.com
Automotive Oil Change Association (AOCA) www.aoca.org
Automotive Parts and Accessories Association (APAA) www.apaa.org
Automotive Service Industry Association (ASIA) www.aftmkt.com
Automotive Services Retailer www.gcipub.com
AutoWeb www.autoweb.com
AutoWeek Online www.autoweek.com
Avatar Corporation www.avatarcorp.com

Badger Lubrication Technologies Inc. www.badgerlubrication.com
Baker Petrolite www.bakerhughes.com/bakerpetrolite
BALLISTOL USA www.ballistol.com
Bardahl Manufacturing Corporation www.bardahl.com
Baron USA Inc. www.baronusa.com
BASF Corporation www.basf.com
Battenfeld Grease and Oil Corporation of New York
www.battenfeld-grease.com
Bayer Corporation www.bayer.com
Bearing.Net www.wearcheck.com
Behnke Lubricants/JAX www.jaxusa.com, www.jax.com

Bell Additives Inc. www.belladditives.com
Bel-Ray Company Inc. www.belray.com
Benz Oil Inc. www.benz.com
Berenfield Containers www.berenfield.com
Bericap NA www.bericap.com
Berry Hinckley Industries www.berry-hinckley.com
Bestolife Corporation www.bestolife.com
BF Goodrich www.bfgoodrich.com
BG Products Inc www.bgprod.com
Bharat Petroleum www.bharatpetroleum.com
Bianco Enterprises Inc. www.bianco.net
Big East Lubricants Inc. www.bigeastlubricants.com
Bijur Lubricating Corporation www.bijur.com
Bio-Rad Laboratories www.bio-rad.com
BioTech International Inc. www.info@biotechintl.com
Bismuth Institute www.bismuth.be
Blackstone Laboratories www.blackstone-labs.com
Blaser Swisslube www.blaser.com
BMW (International) www.bmw.com/bmwe
BMW (USA) www.bmwusa.com
BMW Motorcycles www.bmw-motorrad.com
Bodie-Hoover Petroleum Corporation www.bodie-hoover.com
Boehme Filatex Inc. www.boehmefilatex.com
BoMac Lubricant Technologies Inc. www.bomaclubetech.com
Boncosky Oil Company www.boncosky.com
Boswell Oil Company www.boswelloil.com
BP www.bp.com
BP Amoco Chemicals www.bpamocochemicals.com
BP Lubricants www.bplubricants.com
Brascorp North America Ltd. www.brascorp.on.ca
Brenntag www.brenntag.com
Brenntag Northeast, Inc. www.brenntag.com/
Briner Oil Company www.brineroil.com
British Lubricants Federation Ltd. www.blf.org.uk
British Petroleum (BP) www.bp.com
Britsch Inc. www.britschoil.com
Brno University of Technology, Faculty of Mechanical Engineering,
Elastohydrodynamic Lubrication Research Group <http://fyzika.fme.vutbr.cz/ehd/>
Brugarolas SA www.brugarolas.com/english.htm
Buckley Oil Company www.buckleyoil.com
Buckman Laboratories Inc. www.buckman.com
Buick (GM) www.buick.com
Burlington Chemical www.burco.com
BVA Oils www.bva oils.com

Cabot Corporation (fumed metal oxides) www.cabot-corp.com/cabosil
Cadillac (GM) www.cadillac.com

California Air Resources Board www.arb.ca.gov
Callahan Chemical Company www.calchem.com
Caltex Petroleum Corporation www.caltex.com
Calumet Lubricants Company www.calumetlub.com
Calvary Industries Inc. www.calvaryindustries.com
CAM2 Oil Products Company www.cam2.com
Cambridge <http://chemfinder.camsoft.com>
Cambridge University, Department of Engineering, Tribology
www-mech.eng.cam.ac.uk/Tribology/
Cambridge University, Department of Materials Science and Metallurgy,
Tribology www.msm.cam.ac.uk/tribo/tribol.htm
Canner Associates, Inc. www.canner.com
Cannon Instrument Company www.cannon-ins.com
Capital Enterprises (Power-Up Lubricants) www.NNL690.com
Car and Driver Magazine Online www.caranddriver.com
Cargill — Industrial Oil & Lubricants www.techoil1s.cargill.com
Car-Stuff www.car-stuff.com
Cary Company www.thecarycompany.com
CasChem, Inc. www.cambrex.com
Castle Products Inc. www.castle-comply.com
Castrol Heavy Duty Lubricants, Inc. www.castrolhdl.com
Castrol Industrial North America, Inc. www.castrolindustrialna.com
Castrol International www.castrol.com
Castrol North America www.castrolusa.com
CAT Products Inc. www.run-rite.com
Caterpillar www.cat.com, www.caterpillar.com
Center for Innovation Inc. www.centerforinnovation.com
Center for Tribology, Inc. (CETR) www.cetr.com
Centurion Lubricants www.centurionlubes.com
CEPSA (Spain) www.cepsa.es
Certified Laboratories www.certifiedlaboratories.com
Champion Brands LLC www.championbrands.com
Charles Manufacturing Company www.tsmoly.com
Chart Automotive Group Inc. www.chartauto.com
Chattem Chemicals, Inc. www.chattemchemicals.com
Chem Connect www.chemconnect.com
Chem-Ecol Ltd. www.chem-ecol.com
Chemetall Foote Corporation www.chemetall.com/
Chemical Abstracts Service www.cas.org
Chemical Resources www.chemcenter.org
Chemical Week Magazine www.chemweek.com
Chemicolloid Laboratories Inc. www.colloidmill.com
Chemlube International Inc. www.chemlube.com
Chempet Corp. www.rockvalleyoil.com/chempet.htm
Chemsearch Lubricants www.chemsearch.com
Chemtool Inc./Metalcote www.chemtool.com
Chevrolet (GM) www.chevrolet.com
Chevron www.chevron.com

Chevron Chemical Company www.chevron.com
Chevron Oronite www.chevron.com
Chevron Philips Chemical Company www.chevron.com
Chevron Philips Chemical Company LP www.cpchem.com
Chevron Products Company www.chevron.com
Chevron Products Co. Lubricants & Specialties Products
www.chevron.com/lubricants
Chevron Texaco www.chevrontexaco.com
Christenson Oil www.christensonoil.com
Chrysler (Mercedes Benz) www.chrysler.com
Ciba Specialty Chemicals Corporation www.cibasc.com
CITGO Petroleum Corporation www.citgo.com
Citroen (France) www.citroen.com
Citroen (UK) www.citroen.co.uk/fleet
Clariant Corporation www.clariant.com
Clark Refining and Marketing www.clarkusa.com
Clarkson & Ford Company www.clarkson-ford.com
CLC Lubricants Company www.clclubricants.com
Climax Molybdenum Company www.climaxmolybdenum.com
Coastal Corporation www.elpaso.com
Coastal Unilube Inc. www.coastalunilube.com
Cognis www.cognislubechem.com, www.cognis-us.com, www.cognis.com,
www.na.cognis.com
College of Petroleum and Energy Studies CPS Home Page www.colpet.ac.uk/index.html
College of Petroleum and Energy Studies www.colpet.ac.uk
Colorado Petroleum Products Company www.colopetro.com
Colorado School of Mines Advanced Coating and Surface Engineering
Laboratory (ACSEL) www.mines.edu/research/acsel/acsel.html
Commercial Lubricants Inc. www.comlube.com
Commercial Oil Company, Inc. www.commercialoilcompany.com
Commercial Ullman Lubricants Company www.culc.com
Commonwealth Oil Corporation www.commonwealthoil.com
Como Industrial Equipment Inc. www.comoindustrial.com
Como Lube & Supplies Inc. www.comolube.com
Computational Systems, Inc. www.compsys.com/index.html
Concord Consulting Group Inc. www.concordcg.com
Condat Corporation www.condatcorp.com
Conklin Company, Inc. www.conklin.com
Conoco www.conoco.com
Containment Solutions Inc. www.containmentsolutions.com
Coolants Plus Inc. www.coolantsplus.com
Co-ordinating European Council (CEC) www.cectests.org
Coordinating Research Council (CRC) www.crcao.com
Cortec Corporation www.cortecvci.com
Cosby Oil Company www.cosbyoil.com
Cosmo Oil www.cosmo-oil.co.jp
Country Energy www.countryenergy.com

CPI Engineering Services www.cpieng.com
CRC Industries, Inc. www.crcindustries.com
Creanova, Inc. www.creanovainc.com/
Crescent Manufacturing www.crescentmfg.net
Croda Inc. www.croda.com
Crompton Corporation www.cromptoncorp.com
Cross Oil Refining and Marketing Inc. www.crossoil.com
Crowley Chemical Company Inc. www.crowleychemical.com
Crown Chemical Corporation www.brenntag.com
Crystal Inc-PMC www.pmc-group.com/
CSI www.compsys.com
Cummings-Moore Graphite Company www.cumograph.com
Cummins Engine Company www.cummins.com
Custom Metalcraft Inc. www.custom-metalcraft.com
Cyclo Industries LLC www.cyclo.com

D & D Oil Company, Inc. www.amref.com
D. A. Stuart Company www.d-a-stuart.com
D. B. Becker Company, Inc. www.dbbecker.com
D. W. Davies & Company Inc. www.dwdavies.com
D-A Lubricant Company www.dalube.com
Daimler Chrysler www.daimlerchrysler.com
Danish Technological Institute (DTI) Tribology Centre www.tribology.dti.dk/
Darmex Corporation www.darmex.com
Darsey Oil Company Inc. www.darseyoil.com
David Weber Oil Company www.weberoil.com
Davison Oil Company, Inc. www.davisonoil.com
Dayco Inc. www.dayco.com
DeForest Enterprises Inc. www.deforest.net
Degen Oil and Chemical Company www.eclipse.net/~degen
Delkol www.delkol.co.il
Delphi Automotive Systems www.delphiauto.com
Dennis Petroleum Company, Inc. www.dennispetroleum.com
Department of Defense (DOD) www.dodssp.daps.mil/dodssp.htm
Des-Case Corporation www.des-case.com
Detroit Diesel www.detroitdiesel.com
Deutsches Institute Fur Normung e. V. (DIN) www.din.de
Dexsil Corporation www.dexsil.com
Diagnetics www.entek.com
Dialog www.dialog.com
Diamond Head Petroleum Inc. www.diamondheadpetroleum.com
Diamond Shamrock Refining Company, LP www.udscorp.com
Diesel Progress www.dieselpub.com
Digilube Systems Inc. www.digilube.com
Dingo Maintenance Systems www.dingos.com
Dion & Sons Inc. www.dionandsons.com/
Diversified Petrochemical Services www.chemhelp.com

Dixon Lubricants & Special Products Group, Div. Of Asbury
Carbons www.dixonlube.com
Dodge www.dodge.com
Don Weese Inc. www.schaefferoil.com
Dover Chemical www.doverchem.com
Dow Chemical Company www.dow.com
Dow Corning Corporation www.dowcorning.com
Dryden Oil Company, Inc. www.castrol.com
Dryson Oil Company www.synergynracing.com
DSI Fluids www.dsifluids.com
DSP Technology Inc. www.dspt.com
Dumas Oil Company www.esn.net/dumasoil
DuPont www.dupont.com/intermediates
DuPont — Dow Elastomers www.dupont-dow.com
DuPont Krytox Lubricants www.lubricants.dupont.com
Duro Manufacturing Inc. www.duromanufacturing.com
Dutton — Lainson Company www.dutton-lainson.com
Dylon Industries Inc. www.dylon.com

E. I. DuPont de Nemours and Company www.dupont.com/intermediates
Eagle www.eaglecars.com
Eastech Chemical Inc. www.eastechemical.com
Eastern Oil Company www.easternoil.com
Easy Vac Inc. www.easyvac.com
Ecole Centrale de Lyon, France Laboratoire de Tribologie et Dynamique des
Systèmes www.ec-lyon.fr/recherche/ltds/index.html
Ecole Polytechnique Fédérative de Lausanne, Switzerland <http://igahpse.epfl.ch>
Ecopetrol (Columbian Petroleum Company) www.ecopetrol.com.co
Ecotech Div., Blaster Chemical Companies www.pbblaster.com
Edjean Technical Services Inc. www.edjetech.com
Eidgenössische Technische Hochschule (ETH), Zurich Laboratory for Surface
Science and Technology (LSST) www.surface.mat.ethz.ch/
EKO www.eko.gr
El Paso Corporation www.elpaso.com
The Elco Corporation www.elcocorp.com
Elementis Specialties-Rheox www.rheox.com
Elf Atochem Canada www.atofinachemicals.com
Elf Lubricants North America Inc. www.keystonelubricants.com
Eljay Oil Company, Inc. www.eljayoil.com
Environmental Lubricants Manufacturing Company (ELM) www.elmusa.com
EMERA Fuels Company, Inc. www.emerafuels.com
Emerson Oil Company, Inc. www.emersonoil.com
The Energy Connection www.energyconnect.com
Engel Metallurgical Ltd. www.engelmet.com
Engen Petroleum Ltd. www.engen.co.za
Engineered Composites Inc. www.engineeredcomposites.net
ENI www.eni.it
Environmental and Power Technologies Ltd. www.cleanoil.com

Environmental Lubricants Manufacturing, Inc. (ELM) www.elmusa.com
Environmental Protection Agency (EPA) www.fedworld.gov
Equilon Enterprises LLC www.equilon.com
Equilon Enterprises LLC—Lubricants www.equilonmotivaeequiva.com,
www.shellus.com, www.texaco.com
Ergon Inc. www.ergon.com
Esco Products Inc. www.escopro.com
Esslingen, Technische Akademie www.tae.de
Ethyl Corporation www.ethyl.com
Ethyl Petroleum Additives www.ethyl.com
ETNA Products Inc. www.etna.com
Etna-Bechem Lubricants Ltd. www.etna.com
European Automobile Manufacturers Association (ACEA) www.acea.be
European Oil Companies Organization of E. H. and S. (CONCAWE)
www.concawe.be
European Patent Office www.epo.co.at/epo/
EV1 www.gmev.com
Evans Industries Inc. www.evansind.com
Evergreen Oil www.evergreenoil.com
Exxon www.exxon.com
ExxonMobil Chemical Company www.exxonmobilchemical.com
ExxonMobil Corp. www.exxonmobil.com
ExxonMobil Lubricants & Petroleum Specialties Company
www.exxonmobil.com

F&R Oil Company, Inc. www.froil.com
F. Bacon Industriel Inc. www.f-bacon.com
F.L.A.G. (Fuel, Lubricant, Additives, Grease) Recruiting www.flagsearch.com/
Fachhochschule Hamburg, Germany [www.haw-hamburg.de/fh/forum/f12/
indexf.html/tribologie/etribology.html](http://www.haw-hamburg.de/fh/forum/f12/indexf.html/tribologie/etribology.html)
Falex Corporation www.falex.com
Falex Tribology NV www.falexint.com/
FAMM (Fuel and Marine Marketing) www.fammlc.com/
The Fanning Corporation www.fanncorp.com
Far West Oil Company Inc. www.farwestoil.com
Farmland Industries Inc. www.farmland.com
Federal World www.fedworld.gov
Ferrari www.ferrari.com
Ferro/Keil Chemical www.ferro.com
FEV Engine Technology, Inc. www.fev-et.com/
Fiat www.fiat.com
Fina Oil and Chemical Company www.fina.com
Findett Corporation www.findett.com
Finish Line Technologies Inc. www.finishlineusa.com
FINKE Mineralölwerk www.finke-mineraloel.de
Finnish Oil and Gas Federation www.oil.fi
Flamingo Oil Company www.pinkbird.com
Flo Components Ltd. www.flocomponents.com

Flowtronex International www.flowtronex.com
Fluid Life Corporation www.fluidlife.com
Fluid Systems Partners US Inc. www.fsp-us.com
Fluid Technologies Inc. www.Fluidtechnologies.com
Fluids Analysis Lab www.butler-machinery.com/oil.html
Fluidtec International www.fluidtec.com
Fluitec International www.fluitec.com/
FMC www.fmc.com
FMC Blending & Transfer www.fmcblending-transfer.com
FMC Lithium www.fmclithium.com
Ford Motor Company www.ford.com
Fortum (Finland) www.fortum.com
Forward Corporation www.forwardcorp.com
Freightliner www.freightliner.com
Frontier Performance Lubricants Inc. www.frontierlubricants.com
Fuchs www.fuchs-oil.de
Fuchs Lubricants Company www.fuchs.com
Fuels and Lubes Asia Publications, Inc. www.flasia.com.ph
Fuki America Corporation www.fukiamerica.com
Functional Products www.functionalproducts.com

G–C Lubricants Company www.gclube.com
G & G Oil Co. of Indiana Inc. www.ggoil.com
G. R. O’Shea Company www.groshea.com
G. T. Autochemilube Ltd. www.gta-oil.co.uk
Galactic www.galactic.com
Gamse Lithographing Company www.gamse.com
Gard Corporation www.gardcorp.com
Gas Tops Ltd. www.gastops.com
Gasco Energy www.gascoenergy.com
Gateway Additives www.lubrizol.com
Gear Technology Magazine www.geartechnology.com/mag/gt-index.html
General Motors (GM) www.gm.com
Generation Systems Inc. www.generationsystems.com
Geo. Pfau’s Sons Company, Inc. www.pfauoil.com
Georgia Tech Tribology www.me.gatech.edu/research/tribology.html
Georgia-Pacific Resins, Inc.—Actrachem Division www.gapac.com,
www.gp.com
Gerhardt Inc. www.gerhardths.com
Global Electric Motor Cars, LLC www.gemcar.com
Globetech Services Inc. www.globetech-services.com
Glover Oil Company www.gloversales.com
GMC www.gmc.com
GOA Company www.goanorthcoastoil.com
Gold Eagle Company www.goldeagle.com
Golden Bear Oil Specialties www.goldenbearoil.com
Golden Gate Petroleum www.ggpetrol.com
Goldenwest Lubricants www.goldenwestlubricants.com

Goldschmidt Chemical Corporation www.goldschmidt.com
Gordon Technical Service Company www.gtscfpa.com
Goulston Technologies, Inc. www.goulston.com
Graco Inc. www.graco.com
Granitize Products Inc. www.granitize.com
Greenland Corporation www.greenpluslubes.com
Grignard Company LLC www.purelube.com
Groeneveld Pacific West www.groeneveldpacificwest.com
Gulf Oil www.gulfoil.com

H & W Petroleum Company, Inc. www.hwpetro.com
H. L. Blachford Ltd. www.blachford.ca
H. N. Funkhouser & Company www.hnfunkhouser.com
Haas Corporation www.haascorp.com
Hall Technologies Inc. www.halltechinc.com
Halocarbon Products Corporation www.halocarbon.com
Halon Oil Company, Inc. www.halon.com
Hammonds Fuel Additives, Inc. www.hammondscos.com
Hampel Oil Distributors www.hampeloil.com
Hangsterfer's Laboratories Inc. www.hangsterfers.com
Harry Miller Corporation www.harrymillercorp.com
Hasco Oil Company, Inc. www.hascooil.com
Hatco Corporation www.hatcocorporation.com
Haynes Manufacturing Company www.haynesmfg.com
HCI/Worth Chemical Corporation www.hollandchemical.com
Hedwin Corporation www.hedwin.com
HEF, France www.hef.fr/
Henkel Surface Technologies www.henkel.com, www.thomasregister.com/henkelsurftech
Hercules, Inc., Aqualon Division www.herc.com
Herguth Laboratories Inc. www.herguth.com
Heveatex www.heveatex.com
Hexol Lubricants www.hexol.com
Hindustan Petroleum Corporation, Ltd. www.hindpetro.com
Hino Motor Ltd. www.hino.co.jp
Hi-Port Inc. www.hiport.com
Hi-Tech Industries, Inc. www.hi-techind.com
Holland Applied Technologies www.hollandapt.com
Honda (Japan) www.worldhonda.com
Honda (USA) www.honda.com
Hoosier Penn Oil Company www.hpoil.com
Hoover Materials Handling Group, Inc. www.hooveribcs.com
Horix Manufacturing Company www.sgi.net/horix
Houghton International Inc. www.houghtonintl.com
How Stuff Works www.howstuffworks.com/engine.htm
Howes Lubricator www.howeslube.thomasregister.com
Huls America www.CreanovaInc.com, www.huls.com
Huntsman Corporation www.huntsman.com

Huskey Specialty Lubricants www.huskey.com
Hydraulic Repair & Design, Inc. www.h-r-d.com
Hydrocarbon Asia www.hcasia.safan.com
Hydrocarbon Online www.wearcheck.com/publications.html
Hydrocarbon Processing Magazine www.hydrocarbonprocessing.com/
Hydrosol Inc. www.hydrosol.com
Hydrotex inc. www.hydrotexlube.com
Hy-Per Lube Corporation www.hyperlube.com
Hysitron Incorporated: Nanomechanics www.hysitron.com/
Hyundai www.hyundai-motor.com

I.S.E.L. Inc. www.americansynthol.com
ICIS-LOR Base Oils Pricing Information www.icislol.com/
Idemitsu www.idemitsu.co.jp
ILC/Spectro Oils of America www.spectro-oils.com
Illinois Oil Products, Inc. www.illinoisoilproducts.com
Imperial College, London ME Tribology Section www.me.ic.ac.uk/tribology/
Imperial Oil Company, Inc. www.imperialoil.com
Imperial Oil Ltd. www.imperialoil.ca
Imperial Oil Products and Chemicals Division www.imperialoil.ca
Independent Lubricant Manufacturers Association (ILMA) www.ilm.org
Indian Institute of Science, Bangalore, India, Department of Mechanical Engineering www.mecheng.iisc.ernet.in
Indian Oil Corporation www.indianoilcorp.com
Indiana Bottle Company www.indianabottle.com
Industrial Lubrication and Tribology Journal www.mcb.co.uk/ilt.htm
Industrial Maintenance and Engineering Links (PLI, LLC) [www.memolub.com/link, htm](http://www.memolub.com/link.htm)
Industrial Maintenance & Plant Operation (IMPO) www.mcb.co.uk/cgi-bin/mcb_serve/table1.txt&ilt&stanleaf.htm
Industrial Packing Inc. www.industrialpacking.com
Infineum USA LP www.infineum.com
Infiniti www.infiniti.com
Ingenieria Sales SA de CV www.isalub.com
Inoex Chemical Company www.inoex.com
Insight Services www.testoil.com/
Institut National des Sciences Appliquées de Lyon, France, Laboratoire de Mécanique des Contacts www.insa-lyon.fr/Laboratoires/LMC/index.html
Institute of Materials Inc. (IOM) www.savantgroup.com
Institute of Materials www.savantgroup.com
Institute of Mechanical Engineers (ImechE) www.imeche.org.uk
Institute of Petroleum (IP) <http://212.78.70.142>
Institute of Physics (IOP), Tribology Group www.iop.org
Instruments for Surface Science www.omicron-instruments.com/index.html
Interline Resources Corporation www.interlineresources.com
Internal Energy Agency (IEA) www.iea.org
The International Group Inc. (IGI) www.igiwax.com
International Lubricants Inc. www.lubegard.com

International Organization for Standardization (ISO) www.iso.ch
 International Products Corp. www.ipcol.com
 Intertek Testing Services—Caleb Brett www.itscb.com
 Intl. Tribology Conf. Yokohama 1995 www.mep.titech.ac.jp/Nakahara/jast/itc/itc-home.htm
 Invicta a.s. www.testoil.com/
 Iowa State University, Tribology Laboratory www.eng.iastate.edu/coe/me/research/labs/tribology_lab.html
 IQA Lube Corporation www.iqalube.com
 Irving Oil Corporation www.irvingoil.com
 ISO Translated into Plain English <http://connect.ab.ca/~praxiom>
 Israel Institute of Technology (Technion) <http://meeng.technion.ac.il/Labs/energy.htm#tribology>
 Isuzu www.isuzu.com
 ITW Fluid Products Group www.itwfpg.com

J & H Oil Company www.jhoil.com
 J & S Chemical Corporation www.jschemical.com
 J. H. Calo Company, Inc. www.jhcalo.com
 J. R. Schneider Company, Inc. www.jrschneider.com
 J. A. M. Distributing Company www.jamdistributing.com
 J. B. Chemical Company, Inc. www.jbchemical.com
 J. B. Dewar Inc. www.jbdewar.com
 J. D. Streett & Company, Inc. www.jdstreett.com
 J. N. Abbott Distributor Inc. www.jnabbottdist.com
 Jack Rich Inc. www.jackrich.com
 Jaguar www.jaguarcars.com
 Japan Association of Petroleum Technology (JAPT) www.japt.org
 Japan Automobile Manufacturers Association (JAMA) www.japanauto.com
 Japan Energy Corporation www.j-energy.co.jp/eng/index.html
 Japan Energy www.j-energy.co.jp
 Japanese Society of Tribologists (JAST) (in Japanese) www.jast.or.jp
 Jarchem Industries Inc. www.jarchem.com
 Jasper Engineering & Equipment www.jaspereng.com
 JAX-Behnke Lubricants Inc. www.jax.com
 Jeep www.jeep.com
 Jenkin-Guerin Inc. www.jenkin-guerin.com
 Jet-Lube (UK) Ltd. www.jetlube.com
 John Deere www.deere.com
 Johnson Packings & Industrial Products Inc. www.johnsonpackings.com
 Journal of Fluids Engineering <http://borg.lib.vt.edu/ejournals/JFE/jfe.html>
 Journal of Tribology <http://engineering.dartmouth.edu/thayer/research/index.html>

K.C. Engineering, Ltd. www.kceng.com/
 K.I.S.S. Packaging Systems www.kisspkg.com
 Kafko International Ltd. www.kafkointl.com

Kanazawa University, Japan, Tribology Laboratory <http://web.kanazawa-u.ac.jp/~tribo/labo5e.html>

Kath Fuel Oil Service www.kathfuel.com

Kawasaki www.kawasaki.com, www.khi.co.jp

Keck Oil Company www.keckoil.com

Keil Chemical www.ferro.com

Kelsan Lubricants USA LLC www.kelsan.com

Kem-A-Trix Specialty Lubricants & Compounds www.kematrix.com

Kendall Motor Oil www.kendallmotoroil.com

The Kennedy Group www.kennedygrp.com

King Industries Specialty Chemicals www.kingindustries.com

Kittiwake Developments Limited www.kittiwake.com

Kleenoil Filtration Inc. www.kleenoilfiltrationinc.com

Kleentek-United Air Specialists Inc. www.uasinc.com

Kline & Company Inc. www.klinegroup.com

Kluber Lubrication North America LP www.kluber.com

Koehler Instrument Company www.koehlerinstrument.com

KOST Group Inc. www.kostusa.com

Kruss USA www.krussusa.com

Kuwait National Petroleum Company www.knpc.com.kw

Kyodo Yushi USA Inc. www.kyodoyushi.co.jp

Kyushu University, Japan, Lubrication Engineering Home Page
www.mech.kyushu-u.ac.jp/index.html

Lambent Technologies www.petroferm.com

Lamborghini www.lamborghini.com

Laub/Hunt Packaging Systems www.laubhunt.com

Lawler Manufacturing Corporation www.lawler-mfg.com

Leander Lubricants www.leanderlube.com

Leding Lubricants Inc. www.automatic-lubrication.com

Lee Helms Inc. www.leehelms.com

Leffert Oil Company www.leffertoil.com

Leffler Energy Company www.leffler.com

Legacy Manufacturing www.legacymfg.com

Les Industries Sinto Racing Inc. www.sintoracing.com

Lexus www.lexususa.com

Liftomatic Inc. www.liftomatic.com

Lilyblad Petroleum, Inc. www.lilyblad.com

Lincoln-Mercury www.lincolnmercury.com

Linpac Matls. Handling www.linpacmh.com

Liqua-Tek Inc. www.hdpluslubricants.com

Liqua-Tek/Moraine Packaging www.globaldialog.com/~mpi

Liquid Controls Inc., a Unit of IDEX Corporation www.lcmeter.com

Liquid Horsepower www.holeshot.com/chemicals/additives.html

LithChem International www.lithchem.com

Lockhart Chemical Company www.lockhartchem.com

Loos & Dilworth Inc.—Automotive Division www.loosanddilworth.com

Loos & Dilworth Inc.—Chemical Division www.loosanddilworth.com

Lormar Reclamation Service www.lormar.com
Los Alamos National Laboratory www.lanl.gov/worldview/
Lowe Oil Company/Champion Brands LLC www.championbrands.com
LPS Laboratories www.lpslabs.com
LSST Tribology and Surface Forces <http://bittburg.ethz.ch/LSST/Tribology/default.html>
LSST Tribology Letters <http://bittburg.ethz.ch/LSST/Tribology/letters.html>
Lube Net www.lubenet.com
LubeCon Systems Inc. www.lubecon.com
Lubelink www.lubelink.com
Lubemaster Corporation www.lubemaster.com
LubeNet www.lubenet.com
LubeRos—A Division of Burlington Chemical Company, Inc.
www.luberos.com
Lubes and Greases www.lngpublishing.com
LuBest, Division of Momar Inc. www.momar.com
Lubricant Additives Research www.silverseries.com
Lubricant Technologies www.lubricanttechnologies.com
Lubricants Network Inc. www.lubricantsnetwork.com
Lubricants USA www.finalube.com
Lubricants World www.lubricantsworld.com
Lubrication Engineering Magazine www.stle.org/le_magazine/le_index.htm
Lubrication Engineers Inc. www.le-inc.com
Lubrication Engineers of Canada www.lubeng.com
Lubrication Systems www.lsc.com
Lubrication Technologies Inc. www.lube-tech.com
Lubrication Technology Inc. www.lubricationtechnology.com
Lubrichem International Corporation www.lubrichem.net
Lubriants Distac Inc. www.inspection.gc.ca/english/ppc/reference/n2e.shtml
Lubri-Lab Inc. www.lubrilab.com
LUBRIPLATE Div., Fiske Bros. Refining Company www.lubriplate.com
Lubriport Labs www.ultralabs.com/lubriport
Lubriquip Inc. www.lubriquip.com
Lubritec www.ensenada.net/lubritec/
The Lubrizol Corporation www.lubrizol.com
Lubromation Inc. www.lubromation.com
Lub-Tek Petroleum Products Corporation www.lubtek.com
Lucas Oil Products Inc. www.lucasoil.com
Lukoil (Russian Oil Company) www.lukoil.com
Lulea University of Technology, Department of Mechanical
Engineering www.luth.se/depts/mt/me.html/
Lyondell Lubricants www.lyondelllubricants.com

Machines Production Web Site www.machpro.fr/
Mack Trucks www.macktrucks.com
MagChem Inc. www.magchem.com
Magnalube www.magnalube.com
Maine Lubrication Service Inc. www.maineube.com

MaintenanceWorld www.wearcheck.com
Manor Technology www.manortec.co.uk/
Manor Trade Development Corporation www.amref.com
Mantek Lubricants www.mantek.com
Marathon Ashland Petroleum LLC www.mapllc.com
Marathon Oil Company www.marathon.com
MARC-IV www.marciv.com
Marcus Oil and Chemical www.marcusoil.com
Markee International Corporation www.markee.com
Marly www.marly.com
Maryn International www.poweruplubricants.com
Maryn International Ltd. www.maryngroup.com
Master Chemical Corporation www.masterchemical.com
Master Lubricants Company www.lubriko.com
Maxco Lubricants Company www.maxcolubricants.com
Maxim Industrial Metalworking Lubricants www.maximoil.com
Maxima Racing Lubricants www.maximausa.com
Mays Chemical Company www.mayschem.com
Mazda www.mazda.com
McCollister & Company www.mccollister.com
McGean-Rohco Inc. www.mcgean-rohco.com
McGee Industries Inc. www.888teammclube.com
McIntyre Group Ltd. www.mcintyregroup.com
McLube Divisional/McGee Industries Inc. www.888teammclube.com
Mechanical Engineering Magazine www.memagazine.org/index.html
Mechanical Engineering Tribology Web Site <http://widget.ecn.purdue.edu/~metrib/>
Mega Power Inc. www.megapowerinc.com
Mercedes-Benz (Germany) www.mercedes-benz.de
Metal Forming Lubricants Inc. www.mflube.com
Metal Mates Inc. www.metalmates.net
Metalcote/Chemtool Inc. www.metalcote.com
Metalworking Lubricants www.maximoil.com
Metalworking Lubricants Company www.metalworkinglubricants.com
Metorex Inc. www.metorex.fi
Mettler Toledo www.mt.com
MFA Oil Company www.mfaoil.com
Michel Murphy Enterprises Inc. www.michelmurphy.com
Micro Photonics Inc. www.microphotonics.com/
Mid-Michigan Testing Inc. www.tribologytesting.com
Mid-South Sales Inc. www.mid-southsales.com
Mid-Town Petroleum Inc. www.midtownoil.com
Migdal's Lubricant Web Page <http://members.aol.com/sirmigs/lub.htm>
Milacron Consumable Products Division www.milacron.com
Milatec Corporation www.militec.com
Millennium Lubricants www.millenniumlubricants.com
Miller Oil of Indiana, Inc. www.milleroilinc.com
Mitsubishi Motors www.mitsubishi-motors.co.jp

Mobil www.mobil.com
Mohawk Lubricants Ltd. www.mohawklubes.com
MOL Hungarian Oil & Gas www.mol.hu
Molyduval www.molyduval.com
Molyslip Atlantic Ltd. www.molyslip.co.uk
Monlan Group www.monlangroup.com
Monroe Fluid Technology Inc. www.monroefluid.com
Moore Oil Company www.mooreoil.com
Moraine Packaging Inc. www.hdpluslubricants.com
Morey's Oil Products Company www.moreyonline.com
Moroil Technologies www.moroil.com
Motiva Enterprises LLC www.motivaenterprises.com
Motor Fuels/Combustibles Testing www.empa.ch/englisch/fachber/abt_133/index.htm
Motorol Lubricants www.motorolgroup.com
Motul USA Inc. www.motul.com
Mozel Inc. www.mozel.com
Mr. Good Chem, Inc. www.mrgoodchem.com
Murphy Oil Corporation www.murphyoilcorp.com/
Muscle Products Corporation www.mpc-home.com
Muse, Stancil & Company www.musestancil.com

Nalco Chemical Company www.nalco.com
Nanomechanics and Tribology Swiss Tribology Online
<http://dmxwww.epfl.ch/WWWTRIBO/home.html>
NanoTribometer System www.ume.maine.edu/LASST
Naptec Corporation www.satec.com
NASA Lewis Research Center (LeRC) Tribology & Surface Science
Branch www.lerc.nasa.gov/Other_Groups/SurfSci
National Centre of Tribology, UK www.aeat.com/nct
National Fluid Power Association (NFPA) www.nfpa.com
National Institute for Occupational Safety and Health www.cdc.gov/homepage.html
National Institute of Standards and Technology <http://webbook.nist.gov/chemistry>
National Lubricating Grease Institute (NLGI) www.nlgi.org
National Metal Finishing Resource Center www.nmfrc.org
National Oil Recyclers Association (NORA) www.recycle.net/Associations/rs000141.html
National Petrochemical & Refiners Association www.npradc.org
National Petrochemical Refiners Association (NPR) www.npradc.org
National Petroleum News www.petroretail.net/npn
National Petroleum Refiners Association (NPR) www.npra.org
National Research Council of Canada Lubrication Tribology Services
http://132.246.196.24/en/fsp/service/lubrication_trib.htm
National Resource for Global Standards www.nssn.org
National Tribology Services www.natrib.com

Naval Research Lab Tribology Section—NRL Code 6176
<http://stm2.nrl.navy.mil/~wahl/6176.htm>
NC'eed Enterprises www.backtobasics.com
NCH www.nch.com
Neale Consulting Engineers Limited www.tribology.co.uk/
Neo Synthetic Oil Company Inc. www.neosyntheticoil.com
Newcomb Oil Company www.newcomboil.com
Niagara Lubricant Company, Inc. www.niagaralubricant.com
Niigata University, Japan, Division of Machine Elements Home Page
http://tmtribol.eng.niigata-u.ac.jp/index_e.html
Nissan (Japan) www.nissan.co.jp
Nissan (USA) www.nissandriven.com, www.nissanmotors.com
NOCO Energy Corporation www.noco.com
Noco Lubricants www.noco.com
Nordstom Valves Inc. www.nordstromaudco.com
Noria—Oil Analysis.Com www.oilanalysis.com/
Northern Technologies International Corporation www.ntic.com
Northwestern University, Tribology Lab <http://cset.mech.northwestern.edu/member.htm>
Nyco SA www.nyco.fr
Nye Lubricants www.nyelubricants.com
Nynas Naphthenics www.nynas.com

O'Rourke Petroleum www.orpp.com
Oak Ridge National Laboratory (ORNL) Tribology Test Systems
www.ms.ornl.gov/htmlhome
Oakite Products, Inc. www.oakite.com
OATS (Oil Advisory Technical Services) www.oats.co.uk
Occidental Chemical Corporation www.oxychem.com
Occupational Safety and Health Administration (OSHA) www.osha.gov
Ocean State Oil Inc. www.oceanstateoil.com
Oden Corporation www.oden.thomasregister.com, www.odencorp.com
Ohio State University, Center for Surface Engineering and Tribology,
Gear Dynamics and Gear Noise Research Laboratory [http://gearlab.
eng.ohio-state.edu/](http://gearlab.eng.ohio-state.edu/)
Oil Analysis (Noria) www.oilanalysis.com
Oil Center Research Inc. www.oilcenter.com
Oil Depot www.oildepot.com
Oil Directory.com www.oildirectory.com
Oil Distributing Company www.oildistributing.com
Oil Online www.oilonline.com/
Oil-Chem Research Corporation www.avblend.com
Oilkey Corporation www.oilkey.com
Oil-Link Oil & Gas Online www.oilandgasonline.com
Oilpure Technologies Inc. www.oilpure.com
Oilspot.com www.oilspot.com
OKS Specialty Lubricants www.oks-india.com
OMGI www.omgi.com

OMICRON Vakuumphysik GmbH www.omicron-instruments.com/index.html

Omni Specialty Packaging www.nuvo.cc

OMO Petroleum Company, Inc. www.omoenergy.com

OMS Laboratories, Inc. <http://members.aol.com/labOMS/index.html>

Opel www.opel.com

Orelube Corporation www.orelube.com

Oronite www.oronite.com

O'Rourke Petroleum Products www.orpp.com

Ottsen Oil Company, Inc. www.ottsen.com

Owens-Illinois Inc. www.o-i.com

Oxford Instruments Inc. www.oxinst.com

Paper Systems Inc. www.paper-systems.com

Paramount Products www.paramountproducts.com

PARC Technical Services Inc. www.parctech.com

Parent Petroleum www.parentpetroleum.com

PATCO Additives Division—American Ingredients Company
www.patco-additives.com

Pathfinder Lubricants www.pathfinderlubricants.ca/

Patterson Industries Ltd. (Canada) www.pattersonindustries.com

PBM Services Company www.pbmsc.com

PdMA Corporation www.pdma.com

PDVSA (Venezuela) www.pdvsa.com

PED Inc. www.ped.vianet.ca

Pedroni Fuel Company www.pedronifuel.com

PEMEX (Mexico) www.pemex.com

Pennine Lubricants www.penninelubricants.co.uk

The Pennsylvania State University www.me.psu.edu/research/tribology.html

Pennwell Publications www.pennwell.com

Pennzoil www.pennzoil.com

Pennzoil Industrial Lubricants www.pennzoil.com/prdsmktg/products/industrial/default.htm

Pennzoil-Quaker State Company www.pennzoil-quakerstate.com

PENRECO www.penreco.com

Penta Manufacturing Company/Division of Penta International Corporation www.pentamfg.com

Performance Lubricants & Race Fuels Inc. www.performanceracefuels.com

Perkin Elmer Automotive Research www.perkinelmer.com/ar

Perkins Products Inc. www.perkinsproducts.com

Pertamina (Indonesia) www.pertamina.com

Petro Star Lubricants www.petrostar.com

PetroBlend Corporation www.petroblend.com

Petrobras (Brazil) www.petrobras.com.br

Petro-Canada Lubricants www.htlubricants.com

Petrofind.com www.petrofind.com

Petrogal (Portugal) www.galpenenergia.com/Galp + Energia/home.htm,
www.petrogal.pt

Petrolab Corporation www.petrolab.com
Petrolabs Inc. <http://pages.prodigy.net/petrolabsinc>
Petroleum Analyzer Company LP (PAC) www.Petroleum-Analyzer.com
Petroleum Marketers Association of America (PMAA) www.pmaa.org
Petroleum Packers Inc. www.pepac.com
Petroleum Products Research www.swri.org/4org/d08/petprod/
Petroleum World.com www.petroleumworld.com
Petro-Lubricants Testing Laboratories, Inc. www.pltlab.com
PetroMin Magazine www.petromin.safan.com
PetroMoly, Inc. www.petromoly.com
Petron Corporation www.petroncorp.com
Petroperu (Peru) www.petroperu.com
Petrotest www.petrotest.net
Peugeot www.peugeot.com
Pfaus Sons Company Inc. www.pfauoil.com
Pflaumer Brothers Inc. www.pflaumer.com
Philips Industrial Electronics Deutschland www.philips-tkb.com
Phillips Petroleum Company/Phillips 66 www.phillips66.com/phillips66.asp
Phoenix Petroleum Company www.phoenixpetroleum.com
Pico Chemical Corporation www.picochemical.com
Pilot Chemical Company www.pilotchemical.com
Pinnacle Oil Inc. www.pinnoil.com
Pipeguard of Texas www.pipeguard-texas.com
Pitt Penn Oil Company www.pittpenn.com
Plastic Bottle Corporation www.plasticbottle.com
Plastican Inc. www.plastican.com
Plews/Edelmann Division, Stant Corporation www.stant.com
PLI LLC www.memolub.com
Plint and Partners: Tribology Division www.plint.co.uk/trib.htm
Plymouth www.plymouthcars.com
PMC Specialties Inc. www.pmcsg.com
Polar Company www.polarcompanies.com
Polaris Laboratories, LLC www.polarislabs.com
Polartech Ltd. www.polartech.co.uk
PolySi Technologies www.polysi.com
Pontiac (GM) www.pontiac.com
Power Chemical www.warcopro.com
Power-Up Lubricants www.mayngroup.com
Practicing Oil Analysis Magazine www.practicingoilanalysis.com
Precision Fluids Inc. www.precisionfluids.com
Precision Industries www.precisionind.com
Precision Lubricants www.precisionlubricants.com
PREDICT/DLI—Innovative Predictive Maintenance www.predict-dli.com
Predictive Maintenance Corporation www.pmaint.com/
Predictive Maintenance Corporation: Tribology and the Information Highway www.pmaint.com/tribo/docs/oil_anal/tribo_www.html
Predictive Maintenance Services www.theoilab.com
Premo Lubricant Technologies www.premolube.com

Prime Materials www.primematerials.com
Primrose Oil Company, Inc. www.primrose.com
Probex Corporation www.probex.com
Products Development Manufacturing Company www.veloil.com
ProLab TechnoLub Inc. www.prolab-technologies.com
ProLab-Bio Inc. www.prolab-lub.com
Prolong Super Lubricants www.prolong.com
ProTec International Inc. www.proteclubricants.com
Pulsair Systems Inc. www.pulsair.com
Purac America, Inc. www.purac.com
Purdue University Materials Processing and Tribology Research Group
www.ecn.purdue.edu/~farrist/lab.html
Pure Power Lubricants www.gopurepower.com

QMI www.qminet.com
Quaker Chemical Corporation www.quakerchem.com
Quaker State www qlube.com
Quorpak www.quorpak.com

R & D/Fountain Industries www.fountainindustries.com
R. A. Miller & Company, Inc. www.ramiller.on.ca
R. E. Carroll Inc. www.recarroll.com
R.E.A.L. Services www.realservices.com
R. H. Foster Energy LLC www.rhfoster.com
R. T. Vanderbilt Company www.rtvanderbilt.com
Radian Inc. www.radianinc.com
Radio Oil Company, Inc. www.radiooil.com
Ramos Oil Company, Inc. www.ramosoil.com
Rams-Head Company www.doall.com
Ransome CAT www.ransome.com
Ravenfield Designs Ltd. www.ravenfield.com
Reade Advanced Materials www.reade.com
Red Giant Oil Company www.redgiantoil.com
Red Line Oil www.redlineoil.com
Reed Oil Company www.reedoil.com
Reelcraft Industries Inc. www.realcraft.com
Reit Lubricants Company www.reitlube.com
Reitway Enterprises Inc. www.reitway.com
Reliability Magazine www.pmaint.com/tribo/docs/oil_anal/tribo_www.html
Renewable Lubricants, Inc. www.renewablelube.com
Renite Company www.renite.com
Renite Company-Lubrication Engineers www.renite.com
Renkert Oil www.renkertoil.com
Rensberger Oil Company, Inc. www.rensbergeroil.com
Rexam Closures www.closures.com
Rhein Chemie Corporation www.bayer.com
Rhein Chemie Rheinau GmbH www.rheinchemie.com

Rheotek (PSL SeaMark) www.rheotek.com
Rheox Inc. www.rheox.com
Rhodia www.rhodia.com
Rhone-Poulenc Surfactants & Specialties www.rpsurfactants.com
Ribelin www.ribelin.com
RiceChem, a Division of Stilling Enterprises Inc. www.ricechem.com
RichardsApex Inc. www.richardsapex.com
Riley Oil Company www.rileyoil.com
RO-59 Inc. <http://members.aol.com/ro59inc>
Rock Valley Oil & Chemical Company www.rockvalleyoil.com
Rocol Ltd. www.rocol.com
Rohm & Haas Company www.rohmhaas.com
RohMax Additives GmbH www.rohmax.com
Ross Chem Inc. www.rosschem.com
Rowleys Wholesale www.rowleys.com
Royal Institute of Technology (KTH), Sweden Machine Elements
Home Page www.damek.kth.se/mme
Royal Lubricants Inc. www.royallube.com
Royal Manufacturing Company, Inc. www.royalube.com
Royal Purple, Inc. www.royalpurple.com
Russell-Stanley Corporation www.russell-stanley.com
RWE-DEA (Germany) www.rwe-dea.de
RyDol Products www.rydol.com

Saab www.saab.com
Saab Cars USA www.saabusa.com
Safety Information Resources on the Internet www.siri.org/linksl.html
Safety-Kleen Corporation www.safety-kleen.com
Safety-Kleen Oil Recovery www.ac-rerefined.com
Saftek: Machinery Maintenance Index www.saftek.com/boiler/machine/mmmain.htm
Saitama University, Japan Home Page of Machine Element
Laboratory www.mech.saitama-u.ac.jp/youso/home.html
San Joaquin Refining Company www.sjr.com
Sandia National Laboratories Tribology www.sandia.gov/materials/sciences/
Sandstrom Products Company www.sandstromproducts.com
Sandy Brae Laboratories Inc. www.sandy/brae.com
Santie Oil Company www.santiemidwest.com
Santotrac Traction Lubricants www.santotrac.com
Santovac Fluids Inc. www.santovac.com
Sasol (South Africa) www.sasol.com
SATEC Inc. www.satec.com
Saturn (GM) www.saturncars.com
Savant Group of Companies www.savantgroup.com
Savant Inc. www.savantgroup.com
Saxton Industries Inc. www.saxton.thomasregister.com, www.schaefferoil.com
Scania www.scania.se
Schaeffer Manufacturing www.schaefferoil.com

Schaeffer Oil and Grease www.schaefferoil.com
 Schaeffer Specialized Lubricants www.schaefferoil.com
 Scully Signal Company www.scully.com
 Sea-Land Chemical Company www.sealandchem.com
 Selco Synthetic Lubricants www.synthetic-lubes.com
 Senior Flexonics www.flexonics-hose.com
 Sentry Solutions Ltd. www.sentrysolutions.com
 Service Supply Lubricants LLC www.servicelubricants.com
 Sexton & Peake Inc. www.sexton.qpg.com
 SFR Corporation www.sfrcorp.com
 SGS Control Services Inc. www.sgsgroup.com
 Shamban Tribology Laboratory Kanazawa University, Japan
<http://web.kanazawa-u.ac.jp/~tribo/labo5e.html>
 Shamrock Technologies, Inc. www.shamrocktechnologies.com
 Share Corporation www.sharecorp.com
 Shell (USA) www.shellus.com
 Shell Chemicals www.shellchemical.com
 Shell Global Solutions www.shellglobalsolutions.com
 Shell International www.shell.com/royal-en
 Shell Lubricants (USA) www.shell-lubricants.com
 Shell Oil Products US www.shelloilproductsus.com
 Shepherd Chemical Company www.shepchem.com
 Shrieve Chemical Company www.shrieve.com
 Silvas Oil Company, Inc. www.silvasoil.com
 Silverson Machines Inc. www.silverson.com
 Simons Petroleum Inc. www.simonspetroleum.com
 Sinclair Oil Corporation www.sinclairoil.com
 Sinopec (China Petrochemical Corporation) www.sinopec.com.cn
 SK Corporation (Houston Office) www.skcorp.com
 SKF Quality Technology Centre www.qtc.skf.com
 Sleeveco Inc. www.sleeveco.com
 Slick 50 Corporation www.slick50.com
 Smooth Move Company www.theprojectsthat save.com
 Snyder Industries www.snydernet.com
 Sobit International, Inc. www.sobitinc.com
 Society of Automotive Engineers (SAE) www.sae.org
 Society of Manufacturing Engineers (SME) www.sme.org
 Society of Tribologists and Lubrication Engineers (STLE)
www.stle.org
 Soltex www.soltexinc.com
 Sourdough Fuel www.petrostar.com
 Southern Illinois University, Carbondale Center for Advanced Friction Studies
www.frictioncenter.com
 Southwest Grease Products www.stant.com/brochure.cfm?brochure=155&location_id=119
 Southwest Research Institute www.swri.org
 Southwest Research Institute (SwRI) Engine Technology Section
www.swri.org/4org/d03/engres/engtech

Southwest Spectro-Chem Labs www.swsclabs.com
Southwestern Graphite www.asbury.com
Southwestern Petroleum Corporation (SWEPCO) www.swepco.com,
www.swepcousa.com
SP Morell & Company www.spmorell.com
Spacekraft Packaging www.spacekraft.com
Spartan Chemical Company Inc. Industrial Products Group Division
www.spartanchemical.com
Spartan Oil Company www.spartanonline.com
Specialty Silicone Products Inc. www.sspinc.com
Spectro Oils of America www.goldenspectro.com, www.spectro-oils.com
SpectroInc. Industrial Tribology Systems www.spectroinc.com/
Spectronics Corporation www.spectroline.com
Spectrum Corporation www.spectrumcorporation.com
Spencer Oil Company www.spenceroil.com
Spex CertiPrep Inc. www.spexcsp.com
SQM North America Corporation www.sqmna.com
St. Lawrence Chemicals www.stlawrencechem.com
Star Brite www.starbrite.com
State University of New York, Binghamton Mechanical Engineering
Laboratory www.me.binghamton.edu/me_labs.html
Statoil (Norway) www.statoil.com
Steel Shipping Containers Institute www.steelcontainers.com
Steelco Industrial Lubricants, Inc. www.steelcolubricants.com
Steelco Northwest Distributors www.steelcolubricants.com
Stochem, Inc. www.stochem.com
STP Products Inc. www.stp.com
Stratco Inc. www.stratco.com
SubTech (Petroleum Service & Supply Information)
www.subtech.no/petrlink.htm
Suburban Oil Company, Inc. www.suburbanoil.com
Summit Industrial Products, Inc. www.klsummit.com
Summit Technical Solutions www.lubemanagement.com
Sunnyside Corporation www.sunnysidecorp.com
Sunoco Inc. www.sunocoinc.com
Sunohio, Division of ENSR www.sunohio.com
Superior Graphite Company www.superiorgraphite.com/sgc.nsf
Superior Lubricants Company, Inc. www.superiorlubricants.com
Superior Lubrication Products www.s-l-p.com
Surtec International Inc. www.surtecinternational.com
Swiss Federal Laboratories for Materials Testing and Research (EMPA)
Centre for Surface Technology and Tribology www.empa.ch
Swiss Tribology Online, Nanomechanics and Tribology [http://dmxwww.epfl.
ch/WWWTRIBO/home.html](http://dmxwww.epfl.ch/WWWTRIBO/home.html)
Synco Chemical Corporation www.super-lube.com
SynLube Inc. www.synlube.com
Synthetic Lubricants Inc. www.synlube-mi.com
Syntroleum Corporation www.syntroleum.com

T. S. Moly-Lubricants Inc. www.tsmoly.com
T. W. Brown Oil Company, Inc. www.brownoil.com/soypower.html
Taber Industries www.taberindustries.com
TAI Lubricants www.lubekits.com
Tannas Company www.savantgroup.com
Tannas Company www.savantgroup.com/tannas.sht
TCC www.technicalchemical.com
Technical Chemical Company www.technicalchemical.com
Technical University of Delft, Netherlands Laboratory for Tribology
www.ocp.tudelft.nl/tribo/
Technical University, Munich, Germany www.fzg.mw.tu-muenchen.de
Technische Universitat Ilmenau, Faculty of Mathematics and Natural
Sciences, www.physik.tu-ilmenau.de/index_e.html
Tek-5 Inc. www.tek-5.com
Terresolve Technologies www.terresolve.com
Test Engineering Inc. www.testeng.com
Texaco Inc. www.texaco.com
Texas Refinery Corporation www.texasrefinery.com
Texas Tech University, Tribology www.osci.ttu.edu/ME_Dept/Research/tribology.html
Textile Chemical Company, Inc. www.textilechem.com
Thailand, Petroleum Authority of www.nectec.or.th/users/htk/SciAm/12PTT.html
Thailand, Petroleum Authority www.nectec.or.th
The Maintenance Council www.trucking.org
Thermal-Lube Inc. www.thermal-lube.com
Thermo Elemental www.thermoelemental.com
Thomas Petroleum www.thomaspetro.com
Thornley Company www.thornleycompany.com
Thoughtventions Unlimited Home Page www.tvu.com/%7Ethought/
Tiodize Company, Inc. www.tiodize.com
Titan Laboratories www.titanlab.com
TMC www.truckline.com
Tokyo Institute of Technology, Japan Nakahara Lab. Home page
www.mep.titech.ac.jp/Nakahara/home.html
Tomah Products, Inc. www.tomah3.com
Tom-Pac Inc. www.tom-pac.com
Top Oil Products Company, Ltd. www.topoil.com
Torco International Corporation www.torcoracingoils.com
Tosco www.tosco.com
Total www.total.com, www.totalfinaelf.com/ho/fr/index.htm
Totalfina Oleo Chemicals www.totalfina.com
Tower Oil & Technology Company www.toweroil.com
Toyo Grease Manufacturing (M) SND BHD www.toyogrease.com
Toyota (Japan) www.toyota.co.jp
Toyota (USA) www.toyota.com
TransMontaigne www.transmontaigne.com
Transmountain Oil Company www.transmountainoil.com

TriboLogic Lubricants Inc. www.dynamaxx.com, www.tribologic.com
Tribologist.com www.wearcheck.com/sites.html
Tribology Consultant <http://hometown.aol.com/wearconsul/wear/wear.htm>
Tribology Group www.msm.cam.ac.uk/tribo/tribol.htm
Tribology International www.elsevier.nl/inca/publications/store/3/0/4/7/4
Tribology Letters www.kluweronline.com/issn/1023-8883
Tribology Research Review 1992–1994 www.me.ic.ac.uk/departments/review94/trib/tribreview.html
Tribology Research Review 1995–1997 www.me.ic.ac.uk/departments/review97/trib/tribreview.html
Tribology/Tech-Lube www.tribology.com
Tribos Technologies www.tribostech.com
Trico Manufacturing Corporation www.tricomfg.com
Tricon Specialty Lubricants www.tristrat.com
Trilla Steel Drum Corporation www.trilla.com
Trinity College, Dublin Tribology and Surface Engineering
www.mme.tcd.ie/Groups/Tribology
Troy Corporation www.troycorp.com
Truklink (Truck fleet information) www.truklink.com
Tsinghua University, China, State Key Laboratory of Tribology
www.pim.tsinghua.edu.cn/index_cn.html
TTi's Home Page www.tti-us.com
Turmo Lubrication Inc. www.lubecon.com
TXS Lubricants Inc. www.txsync.com

U.S. Department of Energy (DOE) www.energy.gov
U.S. Department of Transportation (DOT) www.dot.gov
U.S. Energy Information Administration www.eia.doe.gov
U.S. Patent Office www.uspto.gov
U.S. Data Exchange www.usde.com
U.S. Industrial Lubricants Inc. www.usil.cc
U.S. Oil Company, Inc. www.usoil.com
UEC Fuels and Lubrication Laboratories www.uec-usx.com
Ultimate Lubes www.ultimatelubes.com
Ultra Additives, Inc. www.ultraadditives.com
Ultrachem Inc. www.ultracheminc.com
Unilube Systems Ltd. www.unilube.com
Unimark Oil Company www.gardcorp.com
Union Carbide Corporation www.unioncarbide.com
Uniqema www.uniquema.com
Uniroyal Chemical Company Inc. www.uniroyalchemical.com
UniSource Energy Inc. www.unisource-energy.com
Unist, Inc. www.unist.com
Unit Pack Company, Inc. www.unitpack.com
United Color Manufacturing Inc. www.unitedcolor.com
United Lubricants www.unitedlubricants.com
United Oil Company, Inc. www.duralene.com

- United Oil Products Ltd. http://ourworld.compuserve.com/homepages/Ferndale_UK
- United Soybean Board www.unitedsoybean.org
- Universal Lubricants Inc. www.universallubes.com
- University of Akron Tribology Laboratory www.ecgf.uakron.edu/~mech
- University of Applied Sciences (FH-Hamburg), Germany Dept. of Mech. Eng. Tribology www.fh-hamburg.de/fh/fb/m/tribologie/e_index.html
- University of Applied Sciences, Hamburg, Germany, www.haw-hamburg.de/fh/fb/m/tribologie/e_index.html
- University of California, Berkeley Bogey's Tribology Group <http://cml.berkeley.edu/tribo.html>
- University of California, San Diego Center for Magnetic Recording Research <http://orpheus.ucsd.edu/cmrr/>
- University of Florida, Mechanical Engineering Department, Tribology Laboratory <http://grove.ufl.edu/~wgsawyer/>
- University of Illinois, Urbana-Champaign Tribology Laboratory www.mie.uiuc.edu
- University of Kaiserslautern, Germany Sektion Tribologie www.uni-kl.de/en/
- University of Leeds, M.Sc. (Eng.) Course in Surface Engineering and Tribology <http://leva.leeds.ac.uk/tribology/msc/tribmsc.html>
- University of Leeds, UK Research in Tribology <http://leva.leeds.ac.uk/tribology/research.html>
- University of Ljubljana, Faculty of Mechanical Engineering, Center for Tribology and Technical Diagnostics www.ctd.uni-lj.si/eng/ctdeng.htm
- University of Maine Laboratory for Surface Science and Technology (LASST) www.ume.maine.edu/LASST/
- University of Newcastle upon Tyne, UK Ceramics Tribology Research Group www.ncl.ac.uk/materials/materials/resgrps/certrib.html
- University of Northern Iowa www.uni.edu/abil
- University of Notre Dame Tribology/Manufacturing Laboratory www.nd.edu/~ame
- University of Pittsburg, School of Engineering, Mechanical Engineering Department www.engrng.pitt.edu/~mewww
- University of Sheffield, UK Tribology Research Group <http://www.shef.ac.uk/mecheng/tribology/>
- University of Southern Florida, Tribology www.eng.usf.edu/~hess/
- University of Texas at Austin, Petroleum & Geosystems Engineering, Reading Room www.pe.utexas.edu/Dept/Reading/petroleum.html
- University of Tokyo, Japan, Mechanical Engineering Department www.mech.t.u-tokyo.ac.jp/english/index.html
- University of Twente, Netherlands Tribology Group <http://www.wb.utwente.nl/vakgroep/tr/tribeng.htm>
- University of Western Australia Department of Mechanical and Material Engineering <http://www.mech.uwa.edu.au/tribology/>
- University of Western Ontario, Canada Tribology Research Centre <http://www.engga.uwo.ca/research/tribology/Default.htm>
- University of Windsor, Canada Tribology and Wear Research Group <http://zeus.uwindsor.ca/research/wtrg/index.html>

University of Windsor, Canada, Tribology Research Group

<http://venus.uwindsor.ca/research/wtrg/index.html>

Unocal Corporation www.unocal.com

Uppsala University, Sweden Tribology Group <http://www.angstrom.uu.se/materials/index.htm>

USX Engineers & Consultants www.uec.com/labs/ctns

USX Engineers and Consultants: Laboratory Services www.uec.com/labs/

Vacudyne Inc. www.vacudyne.com

Valero Mktg. & Supply www.valero.com

Valhalla Chemical www.valhallachem.com

Valvoline www.valvoline.com

Valvoline Canada www.valvoline.com

Van Horn, Metz & Company, Inc. www.vanhornmetz.com

Vauxhall www.vauxhall.co.uk

Vesco Oil Corporation www.vesco-oil.com

The Victoria Group Inc. www.victoriagroup.com

Viking Pump Inc., a Unit of IDEX Corporation www.vikingpump.com

Vikjay Industries Inc. www.vikjay.com

Virtual Oil Inc. www.virtualoilinc.com

Viswa Lab Corporation www.viswalab.com

Vogel Lubrication System of America www.vogel-lube.com

Volkswagen (Germany) www.vw-online.de

Volkswagen (USA) www.vw.com

Volvo (Sweden) www.volvo.se

Volvo Cars of North America www.volvocars.com

Volvo Group www.volvo.com

Vortex International LLC www.vortexfilter.com

VP Racing Fuels Inc. www.vpracingfuels.com

Vulcan Oil & Chemical Products Inc. www.vulcanoil.com

Vulsay Industries Ltd. www.vulsay.com

Wallace www.wallace.com

Wallover Oil Company www.walloveroil.com

Walthall Oil Company www.walthall-oil.com

Warren Distribution www.wd-wpp.com

Waugh Controls Corporation www.waughcontrols.com

WD-40 Company www.wd40.com

Wear Chat: WearCheck Newsletter www.wearcheck.com/publications.html

Wear www.elsevier.nl/inca/publications/store/5/0/4/1/0/7/

Wearcheck International www.wearcheck.com/

Web-Valu Intl. www.webvalu.com

Wedeven Associated, Inc. <http://members.aol.com/wedeven/>

West Central Soy www.soypower.net

West Penn Oil Company, Inc. www.westpenn.com

Western Michigan University Tribology Laboratory www.mae.wmich.edu/labs/Tribology/Tribology.html

Western Michigan University, Department of Mechanical and Aeronautical Engineering www.mae.wmich.edu/
 Western States Oil www.lubeoil.com
 Western States Petroleum Association www.wspa.org
 Whitaker Oil Company, Inc. www.whitakeroil.com
 Whitmore Manufacturing Company www.whitmores.com, www.whitmore.com
 Wilcox and Flegel Oil Company www.wilcoxandflegel.com
 Wilks Enterprise Inc. www.wilksir.com
 Winfield Brooks Company, Inc. www.tapfree.com
 Winzer Corp. www.winzerusa.com
 Witco (Crompton Corporation) www.witco.com
 Wolf Lake Terminals Inc. www.wolflakeinc.com
 Worcester Polytechnic Institute, Department of Mechanical Engineering www.me.wpi.edu/Research/labs.html
 World Tribologists Database <http://greenfield.fortunecity.com/fish/182/tribologists.htm>
 Worldwide PetroMoly, Inc. www.petro-moly.com
 WSI Chemical Inc. www.wsi-chem-sys.com
 WWW Tribology Information Service www.shef.ac.uk/~mpe/tribology
 WWW Virtual Library: Mechanical Engineering www.vlme.com/
 Wynn Oil Company www.wynnsusa.com

 X-1R Corporation, The www.xlr.com

 Yahoo Lubricants http://dir.yahoo.com/business_and_economy/shopping_and_services/automotive/supplies/lubricants/
 Yahoo Tribology http://ca.yahoo.com/Science/Engineering/Mechanical_Engineering/Tribology/
 Yocum Oil Company, Inc. www.yocumoil.com
 YPF (Argentina) www.ypf.com.ar
 Yuma Industries Inc. www.yumaind.com

 Zimmark Inc. www.zimmark.com
 Zinc Corporation of America www.zinccorp.com

INTERNET LISTINGS BY CATEGORY

Lubricant Fluids (Base Oils, Greases, Biodegradable, Synthetics, Packaged Oils, and Solid Lubricants)

2V Industries Inc. www.2vindustries.com
 49 North www.49northlubricants.com
 76 Lubricants Company www.tosco.com

 A/R Packaging Corporation www.arpackaging.com

 Acculube www.acculube.com

Accurate Lubricants & Metalworking Fluids Inc. (dba Acculube) www.acculube.com

Acheson Colloids Company www.achesonindustries.com

Acme Refining, Division of Mar-Mor Inc. www.acmerefining.com

Acme-Hardesty Company www.acme-hardesty.com

Advanced Ceramics Corporation www.advceramics.com

Advanced Lubrication Specialties Inc. www.advancedlubes.com/

Aerospace Lubricants, Inc. www.aerospacelubricants.com

African Lubricants Industry www.mbendi.co.za/aflu.htm

AG Fluoropolymers USA, Inc. www.fluoropolymers.com

Airosol Company Inc. www.airosol.com

Akzo Nobel www.akzonobel.com

Alco-Metalube Co. www.alco-metalube.com

Alithicon Lubricants, Division of Southeast Oil & Grease Company, Inc. www.alithicon.com

Allegheny Petroleum Products Company www.oils.com

Allen Oil Company www.allenoil.com

Allied Oil & Supply Inc. www.allied-oil.com

Allied Washoe www.alliedwashoe.com

Alpha Grease & Oil Inc. www.arphagrease.thomasregister.com/olc/alpha-grease/

ALT Inc. www.altboron.com

Amalie Oil Company www.amalie.com

Amber Division of Nidera, Inc. www.nidera-us.com

Amcar Inc. www.amcarinc.com

Amerada Hess Corporation www.hess.com

American Agip Company, Inc. www.americanagip.com

American Eagle Technologies Inc. www.frictionrelief.com

American Lubricants Inc. www.americanlubricantsbflco.com

American Lubricating Company www.alcooil.com

American Oil & Supply Company www.aosco.com

American Petroleum Products www.americanpetroleum.com

American Refining Group Inc. www.amref.com

American Synthol Inc. www.americansynthol.com

Amtron Corporation www.superslipperystuff.com/organisation.htm

Amrep Inc. www.amrep.com

AMSOIL Inc. www.amsoil.com

Anderol Specialty Lubricants www.anderol.com

Anti Wear 1 www.dynamicdevelopment.com

Apollo America Corporation www.apolloamerica.com

Aral International www.Aral.com

Arch Chemicals, Inc. www.archbiocides.com

ARCO www.arco.com

Arizona Chemical www.arizonachemical.com

Asbury Carbons, Inc.— Dixon Lubricants www.asbury.com, www.dixonlube.com

Asbury Graphite Mills Inc. www.asbury.com

Asheville Oil Company, Inc. www.ashevilleoil.com

Ashia Denka www.adk.co.jp/eng.htm
Ashland Chemical www.ashchem.com
Ashland Distribution Company www.ashland.com
Aspen Chemical Company www.aspenchemical.com
Associated Petroleum Products www.associatedpetroleum.com
Atlantis International Inc. www.atlantis-usa.com
Atlas Oil Company www.atlasoil.com
ATOFINA Canada Inc. www.atofinacanada.com
Ausimont www.ausiusa.com
Avatar Corporation www.avatarcorp.com

Badger Lubrication Technologies Inc. www.badgerlubrication.com
BALLISTOL USA www.ballistol.com
Battenfeld Grease and Oil Corporation of New York
www.battenfeld-grease.com
Behnke Lubricants/JAX www.jaxusa.com, www.jax.com
Bell Additives Inc. www.belladditives.com
Bel-Ray Company Inc. www.belray.com
Benz Oil Inc. www.benz.com
Berry Hinckley Industries www.berry-hinckley.com
Bestolife Corporation www.bestolife.com
BG Products Inc. www.bgprod.com
Big East Lubricants Inc. www.bigeastlubricants.com
Blaser Swisslube www.blaser.com
Bodie-Hoover Petroleum Corporation www.bodie-hoover.com
Boehme Filatex Inc. www.boehmefilatex.com
BoMac Lubricant Technologies Inc. www.bomaclubetech.com
Boncosky Oil Company www.boncosky.com
Boswell Oil Company www.boswelloil.com
BP Amoco Chemicals www.bpamocochemicals.com
BP Lubricants www.bplubricants.com
Brascorp North America Ltd. www.brascorp.on.ca
Brenntag www.brenntag.com
Brenntag Northeast, Inc. www.brenntag.com/
Briner Oil Company www.brineroil.com
British Petroleum (BP) www.bp.com
Britsch Inc. www.britschoil.com
Brugarolas SA www.brugarolas.com/english.htm
Buckley Oil Company www.buckleyoil.com
BVA Oils www.bva oils.com

Callahan Chemical Company www.calchem.com
Caltex Petroleum Corporation www.caltex.com
Calumet Lubricants Company www.calumetlub.com
Calvary Industries Inc. www.calvaryindustries.com
CAM2 Oil Products Company www.cam2.com
Canner Associates, Inc. www.canner.com

Capital Enterprises (Power-Up Lubricants) www.NNL690.com
Cargill—Industrial Oil & Lubricants www.techoils.cargill.com
Cary Company www.thecarycompany.com
CasChem, Inc. www.cambrex.com
Castle Products Inc. www.castle-comply.com
Castrol Heavy Duty Lubricants, Inc. www.castrolhdl.com
Castrol Industrial North America, Inc. www.castrolindustrialna.com
Castrol International www.castrol.com
Castrol North America www.castrolusa.com
CAT Products Inc. www.run-rite.com
Centurion Lubricants www.centurionlubes.com
Champion Brands LLC www.championbrands.com
Charles Manufacturing Company www.tsmoly.com
Chart Automotive Group Inc. www.chartauto.com
Chem-EcoI Ltd. www.chem-ecol.com
Chemlube International Inc. www.chemlube.com
Chempet Corporation www.rockvalleyoil.com/chempet.htm
Chemsearch Lubricants www.chemsearch.com
Chemtool Inc./Metalcote www.chemtool.com
Chevron Chemical Company www.chevron.com
Chevron Oronite www.chevron.com
Chevron Phillips Chemical Company LP www.cpchem.com
Chevron Phillips Chemical Company www.chevron.com
Chevron Products Company www.chevron.com
Chevron Products Company, Lubricants & Specialties Products
www.chevron.com/lubricants
Christenson Oil www.christensonoil.com
Ciba Specialty Chemicals Corporation www.cibasc.com
Clariant Corporation www.clariant.com
Clark Refining and Marketing www.clarkusa.com
Clarkson & Ford Company www.clarkson-ford.com
CLC Lubricants Company www.clclubricants.com
Climax Molybdenum Company www.climaxmolybdenum.com
Coastal Unilube Inc. www.coastalunilube.com
Cognis www.cognislubechem.com, www.cognis-us.com, www.cognis.com,
www.na.cognis.com
Colorado Petroleum Products Company www.colopetro.com
Commercial Lubricants Inc. www.comlube.com
Commercial Oil Company, Inc. www.commercialoilcompany.com
Commercial Ullman Lubricants Company www.culc.com
Commonwealth Oil Corporation www.commonwealthoil.com
Como Lube & Supplies Inc. www.comolube.com
Condat Corporation www.condatcorp.com
Conklin Company, Inc. www.conklin.com
Coolants Plus Inc. www.coolantsplus.com
Cortec Corporation www.cortecvci.com
Cosby Oil Company www.cosbyoil.com
Country Energy www.countryenergy.com

CPI Engineering Services www.cpieng.com
CRC Industries, Inc. www.crcindustries.com
Crescent Manufacturing www.crescentmfg.net
Crompton Corporation www.cromptoncorp.com
Crown Chemical Corporation www.brenntag.com
Cyclo Industries LLC www.cyclo.com

D & D Oil Company, Inc. www.amref.com
D. A. Stuart Company www.d-a-stuart.com
D. B. Becker Co. Inc. www.dbbecker.com
D. W. Davies & Company, Inc. www.dwdavies.com
D-A Lubricant Company www.dalube.com
Darmex Corporation www.darmex.com
Darsey Oil Company Inc. www.darseyoil.com
David Weber Oil Company www.weberoil.com
Davison Oil Company, Inc. www.davisonoil.com
Dayco Inc. www.dayco.com
Degen Oil and Chemical Company www.eclipse.net/~degen
Delkol www.delkol.co.il
Dennis Petroleum Company, Inc. www.dennispetroleum.com
Diamond Head Petroleum Inc. www.diamondheadpetroleum.com
Diamond Shamrock Refining Company, LP www.udscorp.com
Digilube Systems Inc. www.digilube.com
Dion & Sons Inc. www.dionandsons.com
Dixon Lubricants & Special Products Group, Div. of Asbury Carbons
www.dixonlube.com
Don Weese Inc. www.schaefferoil.com
Dow Chemical Company www.dow.com
Dow Corning Corporation www.dowcorning.com
Dryson Oil Company www.synergynracing.com
Dryden Oil Company, Inc. www.castrol.com
DSI Fluids www.dsifluids.com
Dumas Oil Company www.esn.net/dumasoil
DuPont www.dupont.com/intermediates
DuPont Krytox Lubricants www.lubricants.dupont.com

E. I. DuPont de Nemours and Company www.dupont.com/intermediates
Eastech Chemical Inc. www.eastechchemical.com
Eastern Oil Company www.easternoil.com
Ecotech Div., Blaster Chemical Companies www.pbblaster.com
EKO www.eko.gr
El Paso Corporation www.elpaso.com
Elf Lubricants North America Inc. www.keystonelubricants.com
Eljay Oil Company, Inc. www.eljayoil.com
ELM Environmental Lubricants Manufacturing Company
www.elmusa.com
EMERA Fuels Company, Inc. www.emerafuels.com
Emerson Oil Company, Inc. www.emersonoil.com

Engen Petroleum Ltd. www.engen.co.za
Enichem Americas, Inc. www.eni.it/english/mondo/americhe/usa.html
Environmental Lubricants Manufacturing, Inc. (ELM) www.elmusa.com
Equilon Enterprises LLC www.equilon.com
Equilon Enterprises LLC—Lubricants www.equilonmotivaequiva.com,
www.shellus.com, www.texaco.com
Esco Products Inc. www.escopro.com
ETNA Products Inc. www.etna.com
Etna-Bechem Lubricants Ltd. www.etna.com
Evergreen Oil www.evergreenoil.com
Exxon www.exxon.com
ExxonMobil Chemical Company www.exxonmobilchemical.com
ExxonMobil Lubricants & Petroleum Specialities Company
www.exxonmobil.com

F&R Oil Company, Inc. www.froil.com
F. Bacon Industriel Inc. www.f-bacon.com
FAMM (Fuel and Marine Marketing) www.fammlc.com
Far West Oil Company Inc. www.farwestoil.com
Fina Oil and Chemical Company www.fina.com
Findett Corp. www.findett.com
Finish Line Technologies Inc. www.finishlineusa.com
FINKE Mineraloelwerk www.finke-mineraloel.de
Finnish Oil and Gas Federation www.oil.fi
Flamingo Oil Company www.pinkbird.com
Forward Corporation www.forwardcorp.com
Frontier Performance Lubricants Inc. www.frontierlubricants.com
Fuchs www.fuchs-oil.de
Fuchs Lubricants Company www.fuchs.com
Fuki America Corporation www.fukiamerica.com

G–C Lubricants Company www.gclube.com
G & G Oil Co. of Indiana Inc. www.ggoil.com
G. T. Autochemilube Ltd. www.gta-oil.co.uk
Gard Corporation www.gardcorp.com
Geo. Pfau's Sons Company, Inc. www.pfauoil.com
Georgia-Pacific Pine Chemicals www.gapac.com
Glover Oil Company www.gloversales.com
GOA Company www.goanorthcoastoil.com
Gold Eagle Company www.goldeagle.com
Golden Bear Oil Specialities www.goldenbearoil.com
Golden Gate Petroleum www.ggpetrol.com
Goldenwest Lubricants www.goldenwestlubricants.com
Goldschmidt Chemical Corporation www.goldshmidt.com
Goulston Technologies, Inc. www.goulston.com
Great Lakes Chemical Corporation www.glcc.com
Granitize Products Inc. www.granitize.com

Greenland Corporation www.greenpluslubes.com
Grignard Company LLC www.purelube.com
Groeneveld Pacific West www.groeneveldpacificwest.com
Gulf Oil www.gulfoil.com

H & W Petroleum Company, Inc. www.hwpetro.com
H. L. Blachford Ltd. www.blachford.ca
H. N. Funkhouser & Company www.hnfunkhouser.com
Halocarbon Products Corporation www.halocarbon.com
Halon Oil Company, Inc. www.halon.com
Hampel Oil Distributors www.hampeloil.com
Hangsterfer's Laboratories Inc. www.hangsterfers.com
Harry Miller Corporation www.harrymillercorp.com
Hasco Oil Co. Inc. www.hascooil.com
Hatco Corporation www.hatcocorporation.com
Haynes Manufacturing Company www.haynesmfg.com
HCI/Worth Chemical Corp. www.hollandchemical.com
Henkel Surface Technologies www.henkel.com, www.thomasregister.com/henkelsurftech
Hexol Canada Ltd. www.hexol.com
Hexol Lubricants www.hexol.com
Holland Applied Technologies www.hollandapt.com
Hoosier Penn Oil Company www.hpoil.com
Houghton International Inc. www.houghtonintl.com
Howes Lubricator www.howeslube.thomasregister.com
Huls America www.CreanovaInc.com, www.huls.com
Huskey Specialty Lubricants www.huskey.com
Hydrosol Inc. www.hydrosol.com
Hydrotex Inc. www.hydrotexlube.com
Hy-Per Lube Corporation www.hyperlube.com

I.S.E.L. Inc. www.americansynthol.com
ILC/Spectro Oils of America www.spectro-oils.com
Illinois Oil Products, Inc. www.illinoisoilproducts.com
Imperial Oil Company, Inc. www.imperialoil.com
Imperial Oil Ltd. www.imperialoil.ca
Imperial Oil Products and Chemicals Division www.imperialoil.ca
Ingenieria Sales SA de CV www.isalub.com
Inolex Chemical Company www.inolex.com
International Lubricants Inc. www.lubegard.com
International Products Corporation www.ipcol.com
IQA Lube Corporation www.iqalube.com
Irving Oil Corp www.irvingoil.com
ITW Fluid Products Group www.itwfpg.com

J & H Oil Company www.jhoil.com
J & S Chemical Corporation www.jschemical.com
J. A. M. Distributing Company www.jamdistributing.com

J. B. Chemical Company, Inc. www.jbchemical.com
J. B. Dewar Inc. www.jbdewar.com
J. D. Streett & Company, Inc. www.jdstreett.com
J. N. Abbott Distributor Inc. www.jnabbottdist.com
Jack Rich Inc. www.jackrich.com
Jarchem Industries Inc. www.jarchem.com
Jasper Engineering & Equipment www.jaspereng.com
JAX-Behnke Lubricants Inc. www.jax.com
Jenkin-Guerin Inc. www.jenkin-guerin.com
Jet-Lube (UK) Ltd. www.jetlube.com
Johnson Packings & Industrial Products Inc. www.johnsonpackings.com

Kath Fuel Oil Service www.kathfuel.com
Keck Oil Company www.keckoil.com
Kelsan Lubricants USA LLC www.kelsan.com
Kem-A-Trix Specialty Lubricants & Compounds www.kematrix.com
Kendall Motor Oil www.kendallmotoroil.com
Kluber Lubrication North America LP www.kluber.com
KOST Group Inc. www.kostusa.com
Kyodo Yushi USA Inc. www.kyodoyushi.co.jp

Lambent Technologies www.petroferm.com
LaPorte www.laportepc.com
Leander Lubricants www.leanderlube.com
Lee Helms Inc. www.leehelms.com
Lefferet Oil Company www.leffertoil.com
Les Industries Sinto Racing Inc. www.sintoracing.com
Lilyblad Petroleum, Inc. www.lilyblad.com
Liqua-Tek Inc. www.hdpluslubricants.com
Liquid Horsepower www.holeshot.com/chemicals/additives.html
LithChem International www.lithchem.com
Loos & Dilworth Inc.—Automotive Division www.loosanddilworth.com
Loos & Dilworth Inc.—Chemical Division www.loosanddilworth.com
Lowe Oil Company/Champion Brands LLC www.championbrands.com
LPS Laboratories www.lpslabs.com
LubeCon Systems Inc. www.lubecon.com
Lubemaster Corporation www.lubemaster.com
LubeRos—A Division of Burlington Chemical Company, Inc.
www.luberos.com
LuBest, Division of Momar Inc. www.momar.com
Lubricant Technologies www.lubricanttechnologies.com
Lubricants USA www.finalube.com
Lubrication Engineers Inc. www.le-inc.com
Lubrication Engineers of Canada www.lubeng.com
Lubrication Technologies Inc. www.lube-tech.com
Lubrication Technology Inc. www.lubricationtechnology.com
Lubrichem International Corporation www.lubrichem.net

Lubriants Distac Inc. www.inspection.gc.ca/english/ppc/reference/n2e.shtml
Lubri-Lab Inc. www.lubrilab.com
LUBRIPLATE Div., Fiske Bros. Refining Company www.lubriplate.com
Lubritec www.ensenada.net/lubritec/
Lucas Oil Products Inc. www.lucasoil.com
Lyondell Lubricants www.lyondelllubricants.com

MagChem Inc. www.magchem.com
MagnaLube www.magnalube.com
Maine Lubrication Service Inc. www.mainelube.com
Manor Trade Development Corporation www.amref.com
Mantek Lubricants www.mantek.com
Markee International Corporation www.markee.com
Marly www.marly.com
Maryn International www.poweruplubricants.com
Maryn International Ltd. www.maryngroup.com
Master Chemical Corporation www.masterchemical.com
Master Lubricants Company www.lubriko.com
Maxco Lubricants Company www.maxcolubricants.com
Maxim Industrial Metalworking Lubricants www.maximoil.com
McCollister & Company www.mccollister.com
McGean-Rohco Inc. www.mcgean-rohco.com
McGee Industries Inc. www.888teammclube.com
McLube Divisional/McGee Industries Inc. www.888teammclube.com
Mega Power Inc. www.megapowerinc.com
Metal Forming Lubricants Inc. www.mflube.com
Metal Mates Inc. www.metalmates.net
Metalcote/Chemtool Inc. www.metalcote.com
Metalworking Lubricants www.maximoil.com
Metalworking Lubricants Company www.metalworkinglubricants.com
MFA Oil Company www.mfaoil.com
Mid-South Sales Inc. www.mid-southsales.com
Mid-Town Petroleum Inc. www.midtownoil.com
Milacron Consumable Products Division www.milacron.com
Millennium Lubricants www.millenniumlubricants.com
Miller Oil of Indiana, Inc. www.milleroilinc.com
Mohawk Lubricants Ltd. www.mohawkclubes.com
Molyduval www.molyduval.com
Molyslip Atlantic Ltd. www.molyslip.co.uk
Monroe Fluid Technology Inc. www.monroefluid.com
Moore Oil Company www.mooreoil.com
Moraine Packaging Inc. www.hdpluslubricants.com
Morey's Oil Products Company www.moreyonline.com
Moroil Technologies www.moroil.com
Motiva Enterprises LLC www.motivaenterprises.com
Motorol Lubricants www.motorolgroup.com
Motul USA Inc. www.motul.com

Mr. Good Chem, Inc. www.mrgoodchem.com

Muscle Products Corporation www.mpc-home.com

NCH www.nch.com

Neo Synthetic Oil Company, Inc. www.neosyntheticoil.com

Niagara Lubricant Company, Inc. www.niagaralubricant.com

NOCO Energy Corporation www.noco.com

Noco Lubricants www.noco.com

Nyco SA www.nyco.fr

Nye Lubricants www.nyelubricants.com

Nynas Naphthenics www.nynas.com

O'Rourke Petroleum www.orpp.com

Oakite Products, Inc. www.oakite.com

OATS (Oil Advisory Technical Services) www.oats.co.uk

Occidental Chemical Corporation www.oxychem.com

Ocean State Oil Inc. www.oceanstateoil.com

Oil Center Research Inc. www.oilcenter.com

Oil Center Research International LLC www.oilcenter.com

Oil Depot www.oildepot.com

Oil Distributing Company www.oildistributing.com

Oil-Chem Research Corporation www.avblend.com

Oilkey Corporation www.oilkey.com

Oilpure Technologies Inc. www.oilpure.com

OKS Speciality Lubricants www.oks-india.com

Omega Specialties www.omegachemicalsinc.com

Omni Specialty Packaging www.nuvo.cc

OMO Petroleum Company, Inc. www.omoenergy.com

Orelube Corporation www.orelube.com

Oronite www.oronite.com

O'Rourke Petroleum Products www.orpp.com

Ottsen Oil Company, Inc. www.ottsen.com

Paramount Products www.paramountproducts.com

Parent Petroleum www.parentpetroleum.com

PATCO Additives Division—American Ingredients Company
www.patco-additives.com

Pathfinder Lubricants www.pathfinderlubricants.ca/

PBM Services Company www.pbmsc.com

Pedroni Fuel Company www.pedronifuel.com

Pennine Lubricants www.penninelubricants.co.uk

Pennzoil www.pennzoil.com

Pennzoil Industrial Lubricants [www.pennzoil.com/prdsmktg/products/
industrial/default.htm](http://www.pennzoil.com/prdsmktg/products/industrial/default.htm)

Pennzoil-Quaker State Company www.pennzoil-quakerstate.com

PENRECO www.penreco.com

Penta Manufacturing Company/Division of Penta International Corporation www.pentamfg.com
Performance Lubricants & Race Fuels Inc.
www.performanceracefuels.com
Perkins Products Inc. www.perkinsproducts.com
Petro Star Lubricants www.petrostar.com
PetroBlend Corporation www.petroblend.com
Petro-Canada Lubricants www.htlubricants.com
Petroleum Packers Inc. www.pepac.com
PetroMoly, Inc. www.petromoly.com
Petron Corporation www.petroncorp.com
Pfaus Sons Company Inc. www.pfauoil.com
Pflaumer Brothers Inc. www.pflaumer.com
Phoenix Petroleum Company www.phoenixpetroleum.com
Pico Chemical Corporation www.picochemical.com
Pinnacle Oil Inc. www.pinnoil.com
Pitt Penn Oil Company www.pittpenn.com
Plews/Edelmann Div., Stant Corporation www.stant.com
PolySi Technologies Inc. www.polysi.com
Polar Company www.polarcompanies.com
PolySi Technologies www.polysi.com
Power Chemical www.warcopro.com
Power-Up Lubricants www.mayngroup.com
Precision Fluids Inc. www.precisionfluids.com
Precision Industries www.precisionind.com
Precision Lubricants Inc. www.precisionlubricants.com
Prime Materials www.primematerials.com
Primrose Oil Company Inc. www.primrose.com
Probex Corporation www.probex.com
Products Development Manufacturing Company www.veloil.com
ProLab TechnoLub Inc. www.prolab-technologies.com
ProLab-Bio Inc. www.prolab-lub.com
Prolong Super Lubricants www.prolong.com
ProTec International Inc. www.proteclubricants.com
Pure Power Lubricants www.gopurepower.com

QMI www.qminet.com
Quaker Chemical Corporation www.quakerchem.com
Quaker State www.qlube.com

R. E. Carroll Inc. www.w.recarroll.com
Radio Oil Company Inc. www.radiooil.com
Ramos Oil Company, Inc. www.ramosoil.com
Rams-Head Company www.doall.com
Ransome CAT www.ransome.com
Red Giant Oil Company www.redgiantoil.com
Red Line Oil www.redlineoil.com
Reed Oil Company www.reedoil.com

Reit Lubricants Company www.reitlube.com
Reitway Enterprises Inc. www.reitway.com
Renewable Lubricants, Inc. www.renewablelube.com
Renite Company www.renite.com
Renite Company-Lubrication Engineers www.renite.com
Renkert Oil www.renkertoil.com
Rensberger Oil Company, Inc. www.rensbergeroil.com
RichardsApex Inc. www.richardsapex.com
Riley Oil Company www.rileyoil.com
RO-59 Inc. <http://members.aol.com/ro59inc>
Rock Valley Oil & Chemical Company www.rockvalleyoil.com
Rocol Ltd. www.rocol.com
Rowleys Wholesale www.rowleys.com
Royal Lubricants Inc. www.royallube.com
Royal Manufacturing Company, Inc. www.royalube.com
Royal Purple, Inc. www.royalpurple.com
RyDol Products www.rydol.com

Safety-Kleen Oil Recovery www.ac-rerefined.com
Sandstrom Products Company www.sandstromproducts.com
Santie Oil Company www.santiemidwest.com
Santotrac Traction Lubricants www.santotrac.com
Santovac Fluids Inc. www.santovac.com
Saxton Industries Inc. www.saxton.thomasregister.com,
www.schaefferoil.com
Schaeffer Manufacturing www.schaefferoil.com
Schaeffer Oil and Grease www.schaefferoil.com
Schaeffer Specialized Lubricants www.schaefferoil.com
Selco Synthetic Lubricants www.synthetic-lubes.com
Sentry Solutions Ltd. www.sentrysolutions.com
Service Supply Lubricants LLC www.servicelubricants.com
SFR Corporation www.sfrcorp.com
Share Corporation www.sharecorp.com
Shell Global Solutions www.shellglobalsolutions.com
Shell Lubricants (USA) www.shell-lubricants.com
Shrieve Chemical Company www.shrieve.com
Simons Petroleum Inc. www.simonspetroleum.com
SK Corporation (Houston Office) www.skcorp.com
Slick 50 Corporation www.slick50.com
Smooth Move Company www.theprojectthatsave.com
Sobit International, Inc. www.sobitinc.com
Soltex www.soltextinc.com
Sourdough Fuel www.petrostar.com
Southwest Grease Products www.stant.com/brochure.cfm?brochure=155&location_id=119
Southwestern Graphite www-asbury.com
Southwestern Petroleum Corporation (SWEPCO) www.swepco.com,
www.swepcousa.com

Spartan Chemical Company Inc. Industrial Products Group Division
www.spartanchemical.com
Spartan Oil Company www.spartanonline.com
Specialty Silicone Products Inc. www.sspinc.com
Spectro Oils of America www.goldenspectro.com, www.spectro-oils.com
Spectrum Corporation www.spectrumcorporation.com
Spencer Oil Company www.spenceroil.com
St. Lawrence Chemicals www.stlawrencechem.com
Steelco Industrial Lubricants, Inc. www.steelcolubricants.com
Steelco Northwest Distributors www.steelcolubricants.com
STP Products Inc. www.stp.com
Suburban Oil Company, Inc. www.suburbanoil.com
Summit Industrial Products, Inc. www.klsummit.com
Sunnyside Corporation www.sunnysidecorp.com
Superior Graphite Company www.superiorgraphite.com/sgc.nsf
Superior Lubricants Company, Inc. www.superiorlubricants.com
Superior Lubrication Products www.s-l-p.com
Surtec International Inc. www.surtecinternational.com
Synco Chemical Corporation www.super-lube.com
SynLube Inc. www.synlube.com
Synthetic Lubricants Inc. www.synlube-mi.com
Syntroleum Corporation www.syntroleum.com

T. S. Moly-Lubricants Inc. www.tsmoly.com
T. W. Brown Oil Company, Inc. www.brownoil.com/soypower.html
TAI Lubricants www.lubekits.com
TCC www.technicalchemical.com
Technical Chemical Company www.technicalchemical.com
Tek-5 Inc. www.tek-5.com
Terresolve Technologies www.terresolve.com
Texas Refinery Corporation www.texasrefinery.com
Textile Chemical Company, Inc. www.textilechem.com
Thermal-Lube Inc. www.thermal-lube.com
Thornley Company www.thornleycompany.com
Tiodize Company Inc. www.tiodize.com
Tom-Pac Inc. www.tom-pac.com
Top Oil Products Company, Ltd. www.topoil.com
Torco International Corporation www.torcoracingoils.com
Totalfina Oleo Chemicals www.totalfina.com
Tower Oil & Technology Company www.toweroil.com
Toyo Grease Manufacturing (M) SND BHD www.toyogrease.com
TransMontaigne www.transmontaigne.com
Transmountain Oil Company www.transmountainoil.com
TriboLogic Lubricants Inc. www.dynamaxx.com, www.tribologic.com
Tribos Technologies www.tribotech.com
Trico Manufacturing Corporation www.tricomfg.com
Tricon Specialty Lubricants www.tristrat.com

Turmo Lubrication Inc. www.lubecon.com
TXS Lubricants Inc. www.txsync.com

U. S. Industrial Lubricants Inc. www.usil.cc
U. S. Oil Company, Inc. www.usoil.com
Ultrachem Inc. www.ultracheminc.com
Unimark Oil Company www.gardcorp.com
Union Carbide Corporation www.unioncarbide.com
Uniqema www.uniqema.com
Uniroyal Chemical Company Inc. www.uniroyalchemical.com
UniSource Energy Inc. www.unisource-energy.com
Unist, Inc. www.unist.com
United Lubricants www.unitedlubricants.com
United Oil Company, Inc. www.duralene.com
United Oil Products Ltd. http://ourworld.compuserve.com/homepages/Ferndale_UK
United Soybean Board www.unitedsoybean.org
Universal Lubricants Inc www.universallubes.com
Unocal Corporation www.unocal.com

Valero Mktg. & Supply www.valero.com
Valvoline www.valvoline.com
Valvoline Canada www.valvoline.com
Vesco Oil Corporation www.vesco-oil.com
Vikjay Industries Inc. www.vikjay.com
Virtual Oil Inc. www.virtualoilinc.com
Vogel Lubrication System of America www.vogel-lube.com
VP Racing Fuels Inc. www.vpracingfuels.com
Vulcan Oil & Chemical Products Inc. www.vulcanoil.com

Wallover Oil Company www.walloveroil.com
Walthall Oil Company www.walthall-oil.com
Warren Distribution www.wd-wpp.com
WD-40 Company www.wd40.com
West Central Soy www.soypower.net
Western States Oil www.lubeoil.com
Whitaker Oil Company, Inc. www.whitakeroil.com
Whitmore Manufacturing Company www.whitmores.com,
www.whitmore.com
Wilcox and Flegel Oil Company www.wilcoxandflegel.com
Winfield Brooks Company, Inc. www.tapfree.com
Winzer Coporation www.winzerusa.com
Witco (Crompton Corporation) www.witco.com
Wolf Lake Terminals Inc. www.wolflakeinc.com
Worldwide PetroMoly, Inc. www.petromoly.com
Wynn Oil Company www.wynnsusa.com

X-1R Corp., The www.xlr.com

Yocum Oil Company, Inc. www.yocumoil.com

Yuma Industries Inc. www.yumaind.com

Additives

Acheson Colloids Company www.achesonindustries.com

Acme-Hardesty Company www.acme-hardesty.com

Advanced Lubrication Technology Inc (ALT) www.altboron.com

AFD Technologies www.afdt.com

AG Fluoropolymers USA Inc. www.fluoropolymers.com

Akzo Nobel www.akzonobel.com

Amalie Oil Company www.amalie.com

Amber Division of Nidera, Inc. www.nidera-us.com

American International Chemical www.aicma.com

Amitech www.amitech-usa.com

ANGUS Chemical Company www.dowchemical.com

Anti Wear 1 www.dynamicdevelopment.com

Arch Chemicals, Inc. www.archbiocides.com

Arizona Chemical www.arizonachemical.com

Asbury Carbons, Inc.—Dixon Lubricants www.asbury.com,
www.dixonlube.com

Ashland Distribution Company www.ashland.com

Aspen Chemical Company www.aspenchemical.com

ATOFINA Canada Inc. www.atofinacanada.com

ATOFINA Chemicals, Inc. www.atofina.com

Baker Petrolite www.bakerhughes.com/bakerpetrolite

Bardahl Manufacturing Corporation www.bardahl.com

BASF Corporation www.basf.com

Bayer Corporation www.bayer.com

Bismuth Institute www.bismuth.be

BoMac Lubricant Technologies Inc. www.bomaclubetech.com

BP www.bp.com

BP Amoco Chemicals www.bpamocochemicals.com

Brascorp North America Ltd. www.brascorp.on.ca

British Petroleum (BP) www.bp.com

Buckman Laboratories Inc. www.buckman.com

Burlington Chemical www.burco.com

Cabot Corporation (fumed metal oxides) www.cabot-corp.com/cabosil

Callahan Chemical Company www.calchem.com

Calumet Lubricants Company www.calumetlub.com

Cargill—Industrial Oil & Lubricants www.techoils.cargill.com

Cary Company www.thecarycompany.com

CasChem, Inc. www.cambrex.com

Center for Innovation Inc. www.centerforinnovation.com

Certified Laboratories www.certifiedlaboratories.com

Chattem Chemicals, Inc. www.chattemchemicals.com

Chemetall Foote Corporation www.chemtall.com/
Chemsearch Lubricants www.chemsearch.com
Chevron Oronite www.chevron.com
Ciba Specialty Chemicals Corporation www.cibasc.com
Clariant Corporation www.clariant.com
Climax Molybdenum Company www.climaxmolybdenum.com
Cognis www.cognislubechem.com, www.cognis-us.com,
www.cognis.com, www.na.cognis.com
Commonwealth Oil Corporation www.commonwealthoil.com
Cortec Corporation www.cortecvci.com
Creanova, Inc. www.creanovainc.com/
Croda Inc. www.croda.com
Crompton Corporation www.cromptoncorp.com
Crowley Chemical Company Inc. www.crowleychemical.com
Crown Chemical Corporation www.brenntag.com
Crystal Inc-PMC www.pmc-group.com/
Cummings-Moore Graphite Company www.cumograph.com

D. A. Stuart Company www.d-a-stuart.com
D. B. Becker Company, Inc. www.dbbecker.com
DeForest Enterprises Inc. www.deforest.net
Degen Oil and Chemical Company www.eclipse.net/~degen
Dover Chemical www.doverchem.com
Dover Chemical Company www.doverchem.com
Dow Corning Corporation www.dowcorning.com
DuPont-Dow Elastomers www.dupont-dow.com
Dylon Industries Inc. www.dylon.com

E. I. DuPont de Nemours and Company www.dupont.com/intermediates
E. W. Kaufmann Company www.ewkaufmann.com
The Elco Corporation www.elcocorp.com
Elementis Specialties www.elementis-na.com
Elementis Specialties-Rheox www.rheox.com
Elf Atochem Canada www.atofinachemicals.com
Environmental Lubricants Manufacturing, Inc. (ELM) www.elmusa.com
Ethyl Corporation www.ethyl.com
Ethyl Petroleum Additives www.ethyl.com

The Fanning Corporation www.fanncorp.com
Ferro/Keil Chemical www.ferro.com
FMC www.fmc.com
FMC Lithium www.fmclithium.com
Functional Products www.functionalproducts.com

G. R. O'Shea Company www.groshea.com
Gateway Additives www.lubrizol.com
Geo. Pfau's Sons Company, Inc. www.pfauoil.com
Georgia-Pacific Pine Chemicals www.gapac.com

Georgia-Pacific Resins, Inc.—Atrachem Division

www.gapac.com, www.gp.com

Goldschmidt Chemical Corporation www.goldschmidt.com

Great Lakes Chemical Corporation www.glcc.com

Grignard Company LLC www.purelube.com

Hall Technologies Inc. www.halltechinc.com

Hammonds Fuel Additives, Inc. www.hammondscos.com

Heveatex www.heveatex.com

Holland Applied Technologies www.hollandapt.com

Huntsman Corporation www.huntsman.com

Infineum USA LP www.infineum.com

International Lubricants Inc. www.lubegard.com

J. H. Calo Company, Inc. www.jhcalo.com

J. B. Chemical Company, Inc. www.jbchemical.com

Jarchem Industries Inc. www.jarchem.com

Keil Chemical Division; Ferro Corporation www.ferro.com

King Industries Specialty Chemicals www.kingindustries.com

Lambert Technologies www.petroferm.com

LaPorte www.laportepc.com

Lockhart Chemical Company www.lockhartchem.com

Loos & Dilworth Inc.—Chemical Division www.loosanddilworth.com

LubeRos—A Division of Burlington Chemical Company Inc.

www.luberos.com

Lubricant Additives Research www.silverseries.com

Lubricants Network Inc. www.lubricantsnetwork.com

Lubri-Lab Inc. www.lubrilab.com

The Lubrizol Corporation www.lubrizol.com

Lubrizol Metalworking Additive Company www.lubrizol.com

Mantek Lubricants www.mantek.com

Marcus Oil and Chemical www.marcusoil.com

Master Chemical Corporation www.masterchemical.com

Mays Chemical Company www.mayschem.com

McIntyre Group Ltd. www.mcintyregroup.com

Mega Power Inc. www.megapowerinc.com

Metal Mates Inc. www.metalmates.net

Metalworking Lubricants Company www.metalworkinglubricants.com

Milatec Corporation www.militec.com

Nagase America Corporation www.nagase.com

Naptec Corporation www.satec.com

NC'eed Enterprises www.backtobasics.com

Northern Technologies International Corporation www.ntic.com

Oil Center Research Inc. www.oilcenter.com
OKS Specialty Lubricants www.oks-india.com
Omega Specialties www.omegachemicalsinc.com
OMG Americans Inc. www.omgi.com
OMGI www.omgi.com
Oronite www.oronite.com

PATCO Additives Division—American Ingredients Company
www.patco-additives.com

Pflaumer Brother Inc. www.pflaumer.com
Pilot Chemical Company www.pilotchemical.com
PMC Specialties Inc. www.pmcsg.com
Polartech Ltd. www.polartech.co.uk
Precision Fluids Inc. www.precisionfluids.com
Purac America, Inc. www.purac.com

R. T. Vanderbilt Company Inc. www.rtvanderbilt.com
R. H. Foster Energy LLC www.rhfoster.com
Reade Advanced Materials www.reade.com
Rhein Chemie Corporation www.bayer.com
Rhein Chemie Rheinau GmbH, www.rheinchemie.com
Rheox Inc. www.rheox.com
Rhodia www.rhodia.com
Rhone-Poulenc Surfactants & Specialties www.rpsurfactants.com
RiceChem, A Division of Stilling Enterprises Inc. www.ricechem.com
Rohm & Haas Company www.rohmhaas.com
RohMax Additives GmbH www.rohmax.com
Ross Chem Inc. www.rosschem.com

Santotrac Traction Lubricants www.santotrac.com
Santovac Fluids Inc. www.santovac.com
Sea-Land Chemical Company www.sealandchem.com
Shamrock Technologies, Inc. www.shamrocktechnologies.com
Shell Chemicals www.shellchemical.com
Shepherd Chemical Company www.shepchem.com
Soltex www.soltexinc.com
SP Morell & Company www.spmorell.com
Spartan Chemical Company Inc. Industrial Products Group
Division www.spartanchemical.com
SQM North America Corporation www.sqmna.com
St. Lawrence Chemicals www.stlawrencechem.com
Stochem, Inc. www.stochem.com

Thornley Company www.thornleycompany.com
Tiodize Company, Inc. www.tiodize.com
Tomah Products, Inc. www.tomah3.com
Troy Corporation www.troycorp.com

Ultra Additives Inc. www.ultraadditives.com
Uniqema www.uniqema.com
Uniroyal Chemical Company Inc. www.uniroyalchemical.com
United Color Manufacturing Inc. www.unitedcolor.com
United Lubricants www.unitedlubricants.com

Valhalla Chemical www.valhallachem.com
Van Horn, Metz & Company, Inc. www.vanhornmetz.com
Virtual Oil Inc. www.virtualoilinc.com

Wynn Oil Company www.wynnsusa.com

Zinc Corporation of America www.zinccorp.com

Oil Companies

Adco Petrol Katkiları San Ve. Tic. AS www.adco.com.tr
Amoco www.amoco.com
Aral International www.Aral.com
Asian Oil Company www.nilagems.com/asianoil

Bharat Petroleum www.bharatpetroleum.com
BP www.bp.com

CEPSA (Spain) www.cepsa.es
Chevron www.chevron.com
Chevron Texaco www.chevrontexaco.com
CITGO Petroleum Corporation www.citgo.com
Coastal Corporation www.elpaso.com
Conoco www.conoco.com
Cosmo Oil www.cosmo-oil.co.jp
Cross Oil Refining and Marketing Inc. www.crossoil.com

Ecopetrol (Columbian Petroleum Company) www.ecopetrol.com.co
ENI www.eni.it
Ergon Inc. www.ergon.com
ExxonMobil Corp. www.exxonmobil.com

Fortum (Finland) www.fortum.com

Gasco Energy www.gascoenergy.com

Hindustan Petroleum Corporation, Ltd www.hindpetro.com

Idemitsu www.idemitsu.co.jp
Indian Oil Corporation www.indianoilcorp.com
Interline Resources Corporation www.interlineresources.com

Japan Energy www.j-energy.co.jp

Japan Energy Corporation www.j-energy.co.jp/eng/index.html

Kuwait National Petroleum Company www.knpc.com.kw

Lukoil (Russian Oil Company) www.lukoil.com

Marathon Ashland Petroleum LLC www.mapllc.com

Marathon Oil Company www.marathon.com

Mobil www.mobil.com

MOL Hungarian Oil & Gas www.mol.hu

Murphy Oil Corporation www.murphyoilcorp.com/

PDVSA (Venezuela) www.pdvsa.com

PEMEX (Mexico) www.pemex.com

Pertamina (Indonesia) www.pertamina.com

Petrobras (Brazil) www.petrobras.com.br

Petrogal (Portugal) [www.galpenergia.com/Galp + Energia/home.htm](http://www.galpenergia.com/Galp+Energia/home.htm),
www.petrogal.pt

Petroperu (Peru) www.petroperu.com

Phillips Petroleum Company/Phillips 66 www.phillips66.com/phillips66.asp

RWE-DEA(Germany) www.rwe-dea.de

San Joaquin Refining Company www.sjr.com

Sasol (South Africa) www.sasol.com

Shell (USA) www.shellus.com

Shell International www.shell.com/royal-en

Shell Oil Products US www.shelloilproductsus.com

Sinclair Oil Corporation www.sinclairoil.com

Sinopec (China Petrochemical Corporation) www.sinopec.com.cn

Statoil (Norway) www.statoil.com

Sunoco Inc. www.sunocoinc.com

Texaco Inc. www.texaco.com

Thailand, Petroleum Authority of www.nectec.or.th/users/htk/SciAm/12PTT.html

Tosco www.tosco.com

Total www.total.com, www.totalfinaelf.com/ho/fr/index.htm

YPF (Argentina) www.ypf.com.ar

University Sites

Brno University of Technology, Faculty of Mechanical Engineering, Elastohydrodynamic Lubrication Research Group <http://fyzika.fme.vutbr.cz/ehd/>

Cambridge University, Department of Materials Science and Metallurgy, Tribology www.msm.cam.ac.uk/tribo/tribol.htm

Cambridge University, Department of Engineering, Tribology

www-mech.eng.cam.ac.uk/Tribology

College of Petroleum and Energy Studies CPS Home Page

www.colpet.ac.uk/index.html

College of Petroleum and Energy Studies www.colpet.ac.uk

Colorado School of Mines Advanced Coating and Surface Engineering Laboratory (ACSEL) www.mines.edu/research/acsel/acsel.html

Danish Technological Institute (DTI) Tribology Centre www.tribology.dti.dk/

Ecole Centrale de Lyon, France Laboratoire de Tribologie et Dynamique des Systèmes www.ec-lyon.fr/recherche/ltds/index.html

Ecole Polytechnique Fédérale de Lausanne, Switzerland

<http://igaphse.epfl.ch>

Eidgenössische Technische Hochschule (ETH), Zurich Laboratory for Surface Science and Technology (LSST) www.surface.mat.ethz.ch

Esslingen, Technische Akademie www.tae.de

Fachhochschule Hamburg, Germany www.haw-hamburg.de/fh/forum/fl2/indexf.html/tribologie/etribology.html

Georgia Tech Tribology www.me.gatech.edu/research/tribology.html

Imperial College, London ME Tribology Section www.me.ic.ac.uk/tribology/

Indian Institute of Science, Bangalore, India, Department of Mechanical Engineering www.mecheng.iisc.ernet.in

Institut National des Sciences Appliquées de Lyon, France, Laboratoire de Mécanique des Contacts www.insa-lyon.fr/Laboratories/LMC/index.html

Iowa State University, Tribology Laboratory www.eng.iastate.edu/coe/me/research/labs/tribology_lab.html

Israel Institute of Technology (Technion) <http://meeng.technion.ac.il/Labs/energy.htm#tribology>

Kanazawa University, Japan, Tribology Laboratory

<http://web.kanazawa-u.ac.jp/~tribo/labo5e.html>

Kyushu University, Japan, Lubrication Engineering Home Page

www.mech.kyushu-u.ac.jp/index.html

Luleå University of Technology, Department of Mechanical Engineering www.luth.se/depts/mt/me.html/

Niigata University, Japan, Division of Machine Elements Home Page

http://tmtribol.eng.niigata-u.ac.jp/index_e.html

Northwestern University, Tribology Lab <http://cset.mech.northwestern.edu/member.htm>

Ohio State University, Center for Surface Engineering and Tribology,
Gear Dynamics and Gear Noise Research Laboratory <http://gear-lab.eng.ohio-state.edu>

The Pennsylvania State University www.me.psu.edu/research/tribology.html

Purdue University Materials Processing and Tribology Research Group
www.ecn.purdue.edu/~farrist/lab.html

Purdue University, Mechanical Engineering Tribology Web Site
<http://widget.ecn.purdue.edu/~metrib>

Royal Institute of Technology (KTH), Sweden Machine Elements Home
Page www.damek.kth.se/mme

Saitama University, Japan Home Page of Machine Element
Laboratory www.mech.saitama-u.ac.jp/youso/home.html

Sandia National Laboratories Tribology [www.sandia.gov/
materials/sciences/](http://www.sandia.gov/materials/sciences/)

Shamban Tribology Laboratory Kanazawa University, Japan
<http://web.kanazawa-u.ac.jp/~tribo/labo5e.html>

Southern Illinois University, Carbondale Center for Advanced Friction
Studies www.frictioncenter.com

State University of New York, Binghamton Mechanical Engineering
Laboratory www.me.Binghamton.edu/me_labs.html

Swiss Federal Laboratories for Materials Testing and Research (EMPA)
Centre for Surface Technology and Tribology www.empa.ch

Swiss Tribology Online, Nanomechanics and Tribology
<http://dmxwww.epfl.ch/WWWTRIBO/home.html>

Technical University, Munich, Germany www.fzg.mw.tu-muenchen.de

Technical University of Delft, Netherlands Laboratory for Tribology
www.ocp.tudelft.nl/tribo/

Technische Universitat Ilmenau, Faculty of Mathematics and Natural
Sciences, www.physik.tu-ilmenau.de/index_e.html

Texas Tech University, Tribology [www.osci.ttu.edu/ME_Dept/Research/
tribology.html](http://www.osci.ttu.edu/ME_Dept/Research/tribology.html)

Tokyo Institute of Technology, Japan Nakahara Lab. Home Page
www.mep.titech.ac.jp/Nakahara/home.html

Trinity College, Dublin Tribology and Surface Engineering
www.mme.tcd.ie/Groups/Tribology

Tsinghua University, China, State Key Laboratory
www.pim.tsinghua.edu.cn/index_cn.html

University of Akron Tribology Laboratory www.ecgf.uakron.edu/~mech

University of Applied Sciences, Hamburg, Germany [www.haw-hawburg.de/
fh/fb/m/tribologie/e_index_cn.html](http://www.haw-hawburg.de/fh/fb/m/tribologie/e_index_cn.html)

University of Applied Sciences (FH-Hamburg), Hamburg, Germany Dept. of
Mech. Eng. Tribology [www.fh-hamburg.de/fh/fb/m/tribologie/
e_index_en.html](http://www.fh-hamburg.de/fh/fb/m/tribologie/e_index_en.html)

- University of California, Berkeley Bogey's Tribology Group <http://cml.berkeley.edu/tribo.html>
- University of California, San Diego Center for Magnetic Recording Research <http://orpheus.ucsd.edu/cmrr/>
- University of Florida, Mechanical Engineering Department, Tribology Laboratory <http://grove.ufl.edu/~wgsawyer/>
- University of Illinois, Urbana-Champaign Tribology Laboratory www.mie.uiuc.edu
- University of Kaiserslautern, Germany Sektion Tribologie www.uni-kl.de/en/
- University of Leeds, M.Sc.(Eng). Course in Surface Engineering and Tribology <http://leva.leeds.ac.uk/tribology/msc/tribmsc.html>
- University of Leeds, UK Research in Tribology <http://leva.leeds.ac.uk/tribology/research.html>
- University of Ljubljana, Faculty of Mechanical Engineering, Center for Tribology and Technical Diagnostics www.ctd.uni-lj.si/eng/ctdeng.htm
- University of Maine Laboratory for Surface Science and Technology (LASST) www.ume.maine.edu/LASST/
- University of Maine, NanoTribometer System www.ume.maine.edu/LASST
- University of Newcastle upon Tyne, UK Ceramics Tribology Research Group www.ncl.ac.uk/materials/materials/resgrps/certrib.html
- University of Northern Iowa www.uni.edu/abil
- University of Notre Dame Tribology/Manufacturing Laboratory www.nd.edu/~ame
- University of Pittsburg, School of Engineering, Mechanical Engineering Department www.engrng.pitt.edu/~mewww
- University of Sheffield, UK Tribology Research Group <http://www.shef.ac.uk/mecheng/tribology/>
- University of Southern Florida, Tribology, www.eng.usf.edu/~hess/
- University of Texas at Austin, Petroleum & Geosystems Engineering, Reading Room www.pe.utexas.edu/Dept/Reading/petroleum.html
- University of Tokyo, Japan, Mechanical Engineering Department www.mech.t.u-tokyo.ac.jp/english/index.html
- University of Twente, Netherlands Tribology Group <http://www.wb.utwente.nl/vakgroep/tr/tribeng.htm>
- University of Western Australia Department of Mechanical and Material Engineering <http://www.mech.uwa.edu.au/tribology/>
- University of Western Ontario, Canada Tribology Research Centre <http://www.engga.uwo.ca/research/tribology/Default.htm>
- University of Windsor, Canada, Tribology and Wear Research Group <http://zeus.uwindsor.ca/research/wtrg/index.html>
- University of Windsor, Canada, Tribology Research Group <http://venus.uwindsor.ca/research/wtrg/index.html>
- Uppsala University, Sweden Tribology Group <http://www.angstrom.uu.se/materials/index.htm>
- Western Michigan University Tribology Laboratory www.mae.wmich.edu/labs/Tribology/Tribology.html

Western Michigan University, Department of Mechanical and Aeronautical Engineering. www.mae.wmich.edu
Worcester Polytechnic Institute, Department of Mechanical Engineering
www.me.wpi.edu/Research/labs.html

Government Sites/Industry Sites

American Bearing Manufacturers Association www.abma-dc.org
American Board of Industrial Hygiene www.abih.org
American Carbon Society www.americancarbon society.org
American Chemical Society (ACS) www.acs.org
American Council of Independent Laboratories (ACIL) www.acil.org
American Gear Manufacturers Association (AGMA) www.agma.org
American National Standards Institute (ANSI) www.ansi.org
American Oil Chemists Society (AOCS) www.aocs.org
American Petroleum Institute (API) www.api.org
American Society for Testing and Materials (ASTM) www.astm.org
American Society of Mechanical Engineers International (ASME)
www.asme.org
Argonne National Laboratory www.et.anl.gov
ASTM www.astm.org
Automotive Aftermarket Industry Association (AAIA) www.aftermarket.org
Automotive Oil Change Association (AOCA) www.aoca.org
Automotive Parts and Accessories Association (APAA) www.apaa.org
Automotive Service Industry Association (ASIA) www.aftmkt.com

British Lubricants Federation Ltd. www.blf.org.uk

California Air Resources Board www.arb.ca.gov
Center for Tribology, Inc. (CETR) www.cetr.com
Co-ordinating European Council (CEC) www.cectests.org
Coordinating Research Council (CRC) www.crcao.com

Department of Defense (DOD) www.dodssp.daps.mil/dodssp.htm
Deutsches Institut Für Normung e. V. (DIN) www.din.de

Environmental Protection Agency (EPA) www.fedworld.gov
European Automobile Manufacturers Association (ACEA) www.acea.be
European Oil Companies Organization of E. H. and S. (CONCAWE)
www.concawe.de

Federal World www.fedworld.gov

Independent Lubricant Manufacturers Association (ILMA) www.ilmal.org
Industrial Maintenance & Plant Operation (IMPO) www.mcb.co.uk/cgi-bin/mcb_serve/table1.txt&ilt&/stanleaf.htm
Institute of Materials Inc. (IOM) www.savantgroup.com
Institute of Mechanical Engineers (ImechE) www.imeche.org.uk

Institute of Petroleum (IP) <http://212.78.70.142>
Institute of Physics (IOP), Tribology Group www.iop.org
Internal Energy Agency (IEA) www.iea.org
International Organization for Standardization (ISO) www.iso.ch

Japan Association of Petroleum Technology (JAPT) www.japt.org
Japan Automobile Manufacturers Association (JAMA) www.japanauto.com
Japanese Society of Tribologists (JAST) (in Japanese) www.jast.or.jp

Los Alamos National Laboratory www.lanl.gov/worldview/

NASA Lewis Research Center (LeRC) Tribology & Surface Science
Branch www.lerc.nasa.gov/Other_Groups/Surfsci
National Centre of Tribology, UK www.aeat.com/net
National Fluid Power Association (NFPA) www.nfpa.com
National Institute for Occupational Safety and Health www.cdc.gov/homepage.html
National Institute of Standards and Technology <http://webbook.nist.gov/chemistry>
National Lubricating Grease Institute (NLGI) www.nlgi.org
National Metal Finishing Resource Center www.nmfrc.org
National Oil Recyclers Association (NORA) www.recycle.net/Associations/rs000141.html
National Petrochemical & Refiners Association www.npradc.org
National Petrochemical Refiners Association www.npradc.org
National Petroleum Refiners Association (NPRA) www.npradc.org
National Research Council of Canada Lubrication Tribology Services http://132.246.196.24/en/fsp/service/lubrication_trib.htm
Naval Research Lab Tribology Section—NRL Code 6176
<http://stm2.nrl.navy.mil/~wahl/6176.htm>

Oak Ridge National Laboratory (ORNL) Tribology Test Systems
www.ms.ornl.gov/htmlhome
Occupational Safety and Health Administration (OSHA) www.osha.gov

Petroleum Marketers Association of America (PMAA) www.pmaa.org

Society of Automotive Engineers (SAE) www.sae.org
Society of Manufacturing Engineers (SME) www.sme.org
Society of Tribologists and Lubrication Engineers (STLE) www.stle.org
Southwest Research Institute (SwRI) Engine Technology Section
www.swri.org/4org/d03/engres/engtech/
Southwestern Petroleum Corporation (SWEPCO) www.swepco.com,
www.swepcousa.com

Thailand, Petroleum Authority (PTT) www.nectec.or.th

U.S. Department of Energy (DOE) www.energy.gov
U.S. Department of Transportation (DOT) www.dot.gov

U.S Energy Information Administration www.eia.doe.gov

U.S Patent Office www.uspto.gov

U.S Data Exchange www.used.com

Western States Petroleum Association www.wspa.org

Testing Labs/Equipment/Packaging

A.W. Chesterton Company www.chesterton.com

A/R Packaging Corporation www.arpackaging.com

Accumetric LLC www.accumetric.com

Airflow Systems, Inc. www.airflowsystems.com

Alfa Laval Separation www.alfalaval.com

Allen Filters, Inc. www.allenfilters.com

Ana Laboratories Inc. www.analaboratories.com

Analysts Inc. www.analystinc.com

Anatech Ltd. www.anatechltd.com

Andpak Inc. www.andpak.com

Applied Energy Company www.appliedenergyco.com

Aspen Technology www.aspentech.com/

Associates of Cape Cod Inc. www.acciusa.com

Atico-Internormen-Filter www.atico-internormen.com

Baron USA Inc. www.baronusa.com

Berenfield Containers www.berenfield.com

Bericap NA www.bericap.com

BF Goodrich www.bfgoodrich.com

Bianco Enterprises Inc. www.bianco.net

Bijur Lubricating Corporation www.bijur.com

Biosan Laboratories, Inc. www.biosan.com

Bio-Rad Laboratories www.bio-rad.com

BioTech International Inc. www.info@biotechintl.com

Blackstone Laboratories www.blackstone-labs.com

Cannon Instrument Company www.cannon-ins.com

Certified Laboratories www.certifiedlaboratories.com

Chemicolloid Laboratories Inc. www.colloidmill.com

Como Industrial Equipment Inc. www.comoindustrial.com

Computational Systems, Inc. www.compsys.com/index.html

Containment Solutions Inc. www.containmentsolutions.com

CSI www.compsys.com

Custom Metalcraft Inc. www.custom-metalcraft.com

Delphi Automotive Systems www.delphiauto.com

Des-Case Corporation www.des-case.com

Dexsil Corporation www.dexsil.com

Diagnostics www.entek.com

Digilube Systems Inc. www.digilube.com

Dingo Maintenance Systems www.dingos.com
DSP Technology Inc. www.dspt.com
Duro Manufacturing Inc. www.duromanufacturing.com
Dutton-Lainson Company www.dutton-lainson.com
Dylon Industries Inc. www.dylon.com

Easy Vac Inc. www.easyvac.com
Edjean Technical Services Inc. www.edjetechnical.com
Engel Metallurgical Ltd. www.engelmet.com
Engineered Composites Inc. www.engineeredcomposites.net
Environmental and Power Technologies Ltd. www.cleanoil.com
Evans Industries Inc. www.evansind.com

Falex Corporation www.falex.com
Falex Tribology NV www.falexint.com
FEV Engine Technology, Inc. www.fev-et.com
Flo Components Ltd. www.flocomponents.com
Flowtronex International www.flowtronex.com
Fluid Life Corporation www.fluidlife.com
Fluid Systems Partners US Inc. www.fsp-us.com
Fluid Technologies Inc. www.Fluidtechnologies.com
Fluids Analysis Lab www.butler-machinery.com/oil.html
Fluidtec International www.fluidtec.com
Fluitec International www.fluitec.com/
FMC Blending & Transfer www.fmcblending-transfer.com
Framatome ANP www.framatech.com
Fuel Quality Services Inc. www.fqsgroup.com

G. R. O'Shea Company www.groshea.com
G. T. Autochemilube Ltd. www.gta-oil.co.uk
Galactic www.galactic.com
Gamse Lithographing Company www.gamse.com
Gas Tops Ltd. www.gastops.com
Generation Systems Inc. www.generationsystems.com
Georgia-Pacific Resins, Inc.—Acrachem Division www.gapac.com,
www.gp.com
Gerhardt Inc. www.gerhardths.com
Globetech Services Inc. www.globetech-servies.com
Graco Inc. www.graco.com
Gulfgate Equipment, Inc. www.gulfgateequipment.com

Hedwin Corporation www.hedwin.com
Hercules, Inc., Aqualon Division www.herc.com
Herguth Laboratories Inc. www.herguth.com
Hi-Port Inc. www.hiport.com
Hi-Tech Industries, Inc. www.hi-techind.com
Hoover Materials Handling Group, Inc. www.hooveribcs.com

Horix Manufacturing Company www.sgi.net/horix
Hydraulic Repair & Design, Inc. www.h-r-d.com
Hysitron Incorporated: Nanomechanics www.hysitron.com/

Indiana Bottle Company www.indianabottle.com
Industrial Packing Inc. www.industrialpacking.com
Insight Servies www.testoil.com/
Instruments for Surface Science www.omicron-instruments.com/index.html
Interline Resources Corporation www.interlineresources.com
The International Group Inc. (IGI) www.igiwax.com
Intertek Testing Services-Caleb Brett www.itscb.com
Invicta a.s. www.testoil.com/

J & S Chemical Corporation www.jschemical.com
J. R. Schneider Company, Inc. www.jrschneider.com
JAX-Behnke Lubricants Inc. www.jax.com
Johnson Packings & Industrial Products Inc. www.johnsonpackings.com

K. C. Engineering, Ltd www.kceng.com
K.I.S.S. Packaging Systems www.kisspkg.com
Kafko International Ltd. www.kafkointl.com
The Kennedy Group www.kennedygrp.com
Kittiwake Developments Limited www.kittiwake.com
Kleenoil Filtration Inc. www.kleenoilfiltrationinc.com
Kleentek-United Air Specialists Inc. www.uasinc.com
Koehler Instrument Company www.koehlerinstrument.com
Kruss USA www.krussusa.com

Laub/Hunt Packaging Systems www.laubhunt.com
Lawler Manufacturing Corporation www.lawler-mfg.com
Leding Lubricants Inc. www.automatic-lubrication.com
Legacy Manufacturing www.legacymfg.com
Liftomatic Inc. www.liftomatic.com
Lilyblad Petroleum, Inc. www.lilyblad.com
Linpac Matls. Handling www.linpacmh.com
Liqua-Tek/Moraine Packaging www.globaldialog.com/~mpi
Liquid Controls Inc., A Unit of IDEX Corporation www.lcmeter.com
Lormar Reclamation Service www.lormar.com
LubeCon Systems Inc. www.lubecon.com
Lubricant Technologies www.lubricanttechnologies.com
Lubrication Engineers of Canada www.lubeng.com
Lubrication Systems www.lsc.com
Lubrication Technologies Inc. www.lube-tech.com
Lubriport Labs www.ultralabs.com/lubriport
Lubriquip Inc www.lubriquip.com
The Lubrizol Corporation www.lubrizol.com
Lubromation Inc. www.lubromation.com
Lub-Tek Petroleum Products Corporation www.lubtek.com

Machines Production Web Site www.machpro.fr/
Manor Technology www.manortec.co.uk/
Metalcote/Chemtool Inc. www.metalcote.com
Metorex Inc. www.metorex.fi
Mettler Toledo www.mt.com
Michel Murphy Enterprises Inc. www.michelmurphy.com
Micro Photonics Inc. www.microphotonics.com/
Mid-Michigan Testing Inc. www.tribologytesting.com
Monlan Group www.monlangroup.com
Motor Fuels/Combustibles Testing www.empa.ch/englisch/fachber/abt133/index.htm
Mozel Inc. www.mozel.com

Nalco Chemical Company www.nalco.com
Naptec Corporation www.satec.com
National Tribology Services www.natrib.com
NC'eed Enterprises www.backtobasics.com
NCH www.nch.com
Newcomb Oil Company www.newcomboil.com
Nordstrom Valves Inc. www.nordstromaudco.com

Oden Corporation www.oden.thomasregister.com, www.odencorp.com
Oil Analysis (noria) www.oilanalysis.com
OMICRON Vakuumphysik Gmbh www.omicron-instruments.com/index.html
OMS Laboratories, Inc. <http://members.aol.com/labOMS/index.html>
Owens-Illinois Inc. www.o-i.com
Oxford Instruments Inc. www.oxinst.com

Paper Systems Inc. www.paper-systems.com
PARC Technical Services Inc. www.parctech.com
Patterson Industries Ltd. (Canada) www.pattersonindustries.com
PCS Instruments www.pcs-instruments.com
PdMa Corporation www.pdma.com
PED Inc. www.ped.vianet.ca
Perkin Elmer Automotive Research www.perkinelmer.com/ar
Perkins Products Inc. www.perkinsproducts.com
Perma USA www.permausa.com
Petrolab Corporation www.petrolab.com
Petrolabs Inc. <http://pages.prodigy.net/petrolabsinc>
Petroleum Analyzer Company LP (PAC) www.Petroleum-Analyzer.com
Petroleum Products Research www.swri.org/4org/d08/petprod/
Petro-Lubricants Testing Laboratories, Inc. www.pltllab.com
Petrotest www.petrotest.net
Pflaumer Brothers Inc. www.pflaumer.com
Philips Industrial Electronics Deutschland www.Philips-tkb.com

Pipeguard of Texas www.pieguard-texas.com
Plastic Bottle Corporation www.plasticbottle.com
Plastican Inc. www.plastican.com
Plews/Edelmann Division, Stant Corporation www.stant.com
PLI LLC www.memolub.com
Plint and Partners: Tribology Division www.plint.co.uk/trip.htm
Polaris Laboratories, LLC www.polarislabs.com
PREDICT/DLI—Innovative Predictive Maintenance www.predict-dli.com
Predictive Maintenance Corporation www.pmaint.com/
Predictive Maintenance Services www.theoilab.com
Premo Lubricant Technologies www.premolube.com
Pulsair Systems Inc. www.pulsair.com

Quorpak www.quorpak.com

R & D/Fountain Industries www.fountainindustries.com
R. A. Miller & Company Inc. www.ramiller.on.ca
R.E.A.L. Services www.realservices.com
Radian Inc. www.radianinc.com
Ramos Oil Company Inc. www.ramosoil.com
Ravenfield Designs Ltd. www.ravenfield.com
Reelcraft Industries Inc. www.realcraft.com
Rexam Closures www.closures.com
Rheotek (PSL SeaMark) www.rheotek.com
Ribelin www.ribelin.com
Russell-Stanley Corporation www.russell-stanley.com

Safety-Kleen Corporation www.safety-kleen.com
Saftek:Machinery Maintenance Index www.saftek.com/boiler/machine/mmmain.htm
Sandy Brae Laboratories Inc. www.sandy/brae.com
SATEC Inc. www.satec.com
Savant Group of Companies www.savantgroup.com
Savant Inc. www.savantgroup.com
Saxton Industries Inc. www.saxton.thomasregister.com,
www.schaefferoil.com
Scully Signal Company www.scully.com
Senior Flexonics www.flexonics-hose.com
Service Supply Lubricants LLC www.servicelubricants.com
Sexton & Peake Inc. www.sexton.qpg.com
Silvas Oil Company, Inc. www.silvasoil.com
Silverson Machines Inc. www.silverson.com
Sinclair Oil Corporation www.sinclairoil.com
SKF Quality Technology Center www.qtc.skf.com
Sleeveco Inc. www.sleeveco.com
Snyder Industries www.snydernet.com
Southwest Research Institute www.swri.org

Southwest Spectro-Chem Labs www.swsclabs.com
Spacekraft Packaging www.spacekraft.com
Specialty Silicone Products Inc. www.sspinc.com
SpectroInc. Industrial Tribology Systems www.spectronic.com/
Spectronics Corporation www.spectroline.com
Spex CertiPrep Inc. www.spexcsp.com
Star Brite www.starbrite.com
Steel Shipping Containers Institute www.steelcontainers.com
Stratco Inc. www.stratco.com
Sunohio, Division of ENSR www.sunohio.com
Superior Lubricants Company, Inc. www.superiorlubricants.com

Taber Industries www.taberindustries.com
Tannas Company www.savantgroup.com
Tannas Company www.savantgroup.com/tannas.sht
Thermo Elemental www.thermoelemental.com
Thomas Petroleum www.thomaspetro.com
Thoughtventions Unlimited Home Page www.tvu.com/%7Ethought/
Titan Laboratories www.titanlab.com
Tribologic Lubricants Inc. www.dynamaxx.com, www.tribologic.com
Trico Manufacturing Corporation www.tricomfg.com
Trilla Steel Drum Corporation www.trilla.com
TTi's Home Page www.tti-us.com

UEC Fuels and Lubrication Laboratories www.uec-usx.com
Ultimate Lubes www.ultimatelubes.com
Unilube Systems Ltd. www.unilube.com
Unit Pack Company, Inc. www.unitpack.com
USX Engineers & Consultants www.uec.com/labs/ctns
USX Engineers and Consultants: Laboratory Services www.uec.com/labs/

Vacudyne Inc. www.vacudyne.com
Van Horn, Metz & Company, Inc. www.vanhornmetz.com
Viking Pump Inc., A Unit of IDEX Corporation www.vikingpump.com
Viswa Lab Corporation www.viswalab.com
Vortex International LLC www.vortexfilter.com
Vulsay Industries Ltd. www.vulsay.com

Wallace www.wallace.com
Waugh Controls Corporation www.waughcontrols.com
Wearcheck International www.wearcheck.com
Wedeven Associates, Inc. <http://members.aol.com/wedeven>
West Penn Oil Company, Inc. www.westpenn.com
Wilks Enterprise Inc. www.wilksir.com
WSI Chemical Inc. www.wsi-chem-sys.com

Zimmark Inc. www.zimmark.com

Car/Truck Manufacturers

Alfa Romeo www.alfaromeo.com

Audi www.audi.com

BMW (International) www.bmw.com/bmwe

BMW(USA) www.bmwusa.com

BMW Motorcycles www.bmw-motorrad.com

Buick (GM) www.buick.com

Cadillac (GM) www.cadillac.com

Caterpillar www.cat.com, www.caterpillar.com

Chevrolet (GM) www.chevrolet.com

Chrysler (Mercedes Benz) www.chrysler.com

Citroen (France) www.citroen.com

Citroen (UK) www.citroen.co.uk/fleet

Cummins Engine Company www.cummins.com

Daimler Chrysler www.daimlerchrysler.com

Detroit Diesel www.detroitdiesel.com

Dodge www.dodge.com

Eagle www.eaglecars.com

EV1 www.gmev.com

Ferrari www.ferrari.com

Fiat www.fiat.com

Ford Motor Company www.ford.com

General Motors (GM) www.gm.com

Global Electric Motor Cars, LLC www.gemcar.com

Hyundai www.hyundai-motor.com

Infiniti www.infiniti.com

Isuzu www/isuzu.com

Jaguar www.jaguarcars.com

Jeep www.jeep.com

John Deere www.deere.com

Kawasaki www.kawasaki.com, www.khi.co.jp

Lamborghini www.lamborghini.com

Lexus www.lexususa.com

Lincoln-Mercury www.lincolnmercury.com

Mack Trucks www.macktrucks.com
 Mazda www.mazda.com
 Mercedes-Benz (Germany) www.mercedes-benz.de
 Mitsubishi Motors www.mitsubishi-motors.co.jp

 Nissan (Japan) www.nissan.co.jp
 Nissan (USA) www.nissandriven.com, www.nissanmotors.com

 Opel www.opel.com

 Peugeot www.peugeot.com
 Plymouth www.plymouthcars.com
 Pontiac (GM) www.pontiac.com

 Saab www.saab.com
 Saab Cars USA www.saabusa.com
 Saturn (GM) www.saturncars.com
 Scania www.scania.se

 Toyota (Japan) www.toyota.co.jp
 Toyota (USA) www.toyota.com

 Vauxhall www.vauxhall.co.uk
 Volkswagen (Germany) www.vw-online.de
 Volkswagen (USA) www.vw.com
 Volvo (Sweden) www.volvo.se
 Volvo Cars of North America www.volvocars.com
 Volvo Group www.volvo.com

Publications/References/Recruiting/Search Tools, etc.

American Machinist www.penton.com/cgi-bin/superdirectory/details.pl?id=317
 API Links www.api.org/links
 Automotive & Industrial Lubricants Guide www.wearcheck.com
 Automotive & Industrial Lubricants Guide by David Bradbury
www.escape.ca/~dbrad/index.htm
 Automotive & Industrial Lubricants Tutorial www.escape.ca/~dbrad/index.htm
 Automotive News www.autonews.com
 Automotive Service Industry Association (ASIA) www.aftmkt.com/asia
 Automotive Services Retailer www.gcipub.com
 AutoWeb www.autoweb.com
 AutoWeek Online www.autoweek.com

 Bearing.Net www.wearcheck.com

 Cambridge <http://chemfinder.camsoft.com>
 Car and Driver Magazine Online www.caranddriver.com

Car-Stuff www.car-stuff.com

Center for Innovation Inc. www.centerforinnovation.com

Chem Connect www.chemconnect.com

Chemical Abstracts Service www.cas.org

Chemical Resources www.chemcenter.org

Chemical Week Magazine www.chemweek.com

Concord Consulting Group Inc. www.concordcg.com

Dialog www.dialog.com

Diesel Progress www.dieselpub.com

Diversified Petrochemical Services www.chemhelp.com

The Energy Connection www.energyconnect.com

European Patent Office www.epo.co.at/epo/

F.L.A.G (Fuel, Lubricant, Additives, Grease) Recruiting www.flagsearch.com/

Farmland Industries Inc. www.farmland.com

Fuel Quest www.fuelquest.com/cgi-bin/fuelqst/corporate/fq_index.jsp

Fuels and Lubes Asia Publications, Inc. www.flasia.com.ph

Gear Technology Magazine www.geartechnology.com/mag/gt-index.html

Haas Corporation www.haascorp.com

HEF, France www.hef.fr/

How Stuff Works www.howstuffworks.com/engine.htm

Hydrocarbon Asia www.hcasia.safan.com

Hydrocarbon Online www.wearcheck.com/publications.html

Hydrocarbon Processing Magazine www.hydrocarbonprocessing.com/

ICIS-LOR Base Oils Pricing Information www.icislors.com/

Industrial Lubrication and Tribology Journal www.mcb.co.uk/ilt.htm

Industrial Maintenance and Engineering Links (PLI. LLC) www.memolub.com/link.htm

Intl. Tribology.Conf. Yokohama. 1995 www.mep.titech.ac.jp/Nakahara/jast/itc/itc-home.htm

ISO Translated into Plain English <http://connect.ab.ca/~praxiom>

Journal of Fluids Engineering <http://borg.lib.vt.edu/ejournals/JFE/jfe.html>

Journal of Tribology <http://engineering.dartmouth.edu/thayer/research/index.html>

Kline & Company Inc. www.klinegroup.com

LSST Tribology and Surface Forces <http://bittburg.ethz.ch/LSST/Tribology/default.html>

LSST Tribology Letters <http://bittburg.ethz.ch/LSST/Tribology/letters.htm>
Lube Net www.lubenet.com
Lubelink www.lubelink.com
Lubes and Greases www.lngpublishing.com
Lubricants Network Inc. www.lubricantsnetwork.com
Lubricants World www.lubricantsworld.com
Lubrication Engineering Magazine www.stle.org/le_magazine/le_index.htm

Maintenance World www.wearcheck.com
MARC-IV www.marciv.com
Mechanical Engineering Magazine www.memagazine.ofg/index.html
Migdal's Lubricant Web Page <http://members.aol.com/sirmigs/lub.htm>
Muse, Stancil & Company www.musestancil.com

National Petroleum News www.petroretail.net/npn
National Resource for Global Standards www.nssn.org
Neale Consulting Engineers Limited www.tribology.co.uk/
Noria—OilAnalysis.Com www.oilanalysis.com/

Oil Directory.com www.oildirectory.com
Oil Online www.oilonline.com/
Oil-Link Oil & Gas Online www.oilandgasonline.com
Oilspot.com www.oilspot.com

Pennwell Publications www.pennwell.com
Petrofind.com www.petrofind.com
Petroleum World.com www.petroleumworld.com
PetroMin Magazine www.petromin.safan.com
Practicing Oil Analysis Magazine www.practicingoilanalysis.com
Predictive Maintenance Corporation: Tribology and the Information
Highway www.pmaint.com/tribo/docs/oil_anal/tribo_www.htmlref

Reliability Magazine www.pmaint.com/tribo/docs/oil_anal/tribo_www.html

Safety Information Resources on the Internet www.siri.org/links.html
Savant Group of Companies www.savantgroup.com
SGS Control Services Inc. www.sgsgroup.com
Shell Global Solutions www.shellglobalsolutions.com
SubTech (Petroleum Service & Supply Information) www.subtech.no/petrlink.htm
Summit Technical Solutions www.lubemanagement.com
Sunohio, Division of ENSR www.sunohio.com

Tannas Company www.savantgroup.com
Test Engineering Inc. www.testeng.com
The Maintenance Council www.trucking.org
TMC www.truckline.com

Tribologist.com www.wearcheck.com/sites.html
Tribology Consultant <http://hometown.aol.com/wearconsul/wear/wear.htm>
Tribology International www.elsevier.nl/inca/publications/store/3/0/4/7/4
Tribology Letters www.kluweronline.com/issn/1023-8883
Tribology Research Review 1992–1994 www.me.ic.ac.uk/departments/review94/trib/tribreview.html
Tribology Research Review 1995–1997 www.me.ic.ac.uk/departments/review97/trib/tribreview.html
Tribology/Tech-Lube www.tribology.com
Trucklink (truck fleet information) www.truklink.com

United Soybean Board www.unitedsoybean.org

The Victoria Group Inc. www.victoriagroup.com

Wear Chat: WearCheck Newsletter www.wearcheck.com/publications.html
Wear www.elsevier.nl/inca/publications/store/5/0/4/1/0/7
World Tribologists Database <http://greenfield.fortunecity.com/fish/182/tribologists.htm>
www Tribology Information Service www.shef.ac.uk/~mpe/tribology/
www Virtual Library: Mechanical Engineering www.vlme.com/

Yahoo Lubricants http://dir.yahoo.com/business_and_economy/shopping_and_services/automotive/supplies/lubricants/
Yahoo Tribology http://ca.yahoo.com/Science/Engineering/Mechanical_Engineering/Tribology/

about the book . . .

This reference examines the mechanisms, functions, advantages, and limitations of lubricant additives such as antioxidants, antiwear agents, detergents and dispersants, friction modifiers, and metalworking fluids for decreased wear, rust, breakdown, swelling, and deposits in machinery and engines—detailing the design of cost-effective, environmentally friendly lubricant technologies and components for the automotive, industrial, manufacturing, and aerospace industries.

Contains a CD-ROM with links to current Internet resources for the lubricant industry.

Lubricant Additives presents methods to improve the performance and stability of lubricants...protect metal surfaces against wear...control deposits and contaminants such as wear debris, sludge, acids, and peroxides...select lubricant additives for the food industry...choose the most appropriate ashless additives...avoid microbial degradation...and lower toxicity...and describes standard lubricant test methods and product specifications...the mechanisms of action and benefits of specific types of lubricant additives...and recent industry trends.

about the editor . . .

LESLIE R. RUDNICK is Senior Scientist at The Energy Institute, The Pennsylvania State University, University Park. The author, coauthor, editor, or coeditor of over 65 journal articles, book chapters, and books, including *Synthetic Lubricants and High-Performance Functional Fluids, Second Edition* (Marcel Dekker, Inc.), he holds 29 patents and is a member of the Society of Tribologists and Lubrication Engineers, the American Chemical Society, the American Society for Testing and Materials, and the Society of Automotive Engineers. Dr. Rudnick serves on the editorial board of the *Journal of Synthetic Lubrication* and received the B.S. degree (1969) in chemistry from the University of Iowa, Iowa City, and the M.S. (1972) and Ph.D. (1975) degrees in chemistry from Rutgers University, New Brunswick, New Jersey.

Printed in the United States of America



CRC Press

Taylor & Francis Group
an informa business

www.taylorandfrancisgroup.com

6000 Broken Sound Parkway, NW
Suite 300, Boca Raton, FL 33487
270 Madison Avenue
New York, NY 10016
2 Park Square, Milton Park
Abingdon, Oxon OX14 4RN, UK

DK2036

ISBN 0-8247-0857-1



9 780824 708573



90000